LXX. *A Two-crystal Moving Film Spectrometer for Comparative Intensity Measurements in X-Ray Crystal Analysis.* By J. MONTEATH ROBERTSON, *M.A., Ph.D., D.Sc.**

[Plates XV. & XVI.]

1. *General Description.*

THE photographic method of measuring the integrated intensities of X-ray crystal reflexions † has been greatly developed in the past few years, and while it is now comparable in accuracy to the ionization chamber method, for some purposes it has definite advantages. For example, a large number of reflexions may be recorded on one film in one operation, by increasing the exposure time excessively weak reflexions may be registered, and there is no chance of missing any reflexion within the region explored. These are important considerations when a complete crystal analysis is desired.

For absolute measurements it has in the past been necessary to employ the ionization chamber method, and at a later stage correlate the results so obtained

* Communicated by the Author.

† Compare B. W. Robinson, J. Sci. Instr. x. p. 233 (1933). The method referred to throughout this paper is that of the small single crystal completely immersed in the X-ray beam. Other methods dealing with an extended crystal face, etc., are not considered.

with the more detailed photographic measurements. There is no objection to this procedure if all the apparatus required is available, and further, if the actual crystal specimens upon which absolute measurements have been made are sufficiently permanent to be used again in the photographic work, or at least as sub-standards in such work. Otherwise appreciable errors are likely owing to the varying degrees of perfection of the specimens, particularly in the case of the strong reflexions which are usually employed for absolute measurements.

The first object of the instrument described below is to render the process of absolute measurement, by comparison with accurately known standards, entirely photographic. The most obvious method of doing this would be to rotate the standard crystal and the crystal to be measured side by side in the same X-ray beam. Apart from the difficulty of mounting the crystals in this way, there are two objections to such a process. In the first place it would be difficult to ensure that the X-ray beam had uniform intensity over the regions occupied by the two crystals ; and secondly, the positions on the film of the reflexions from the two crystals would sometimes coincide and lead to confusion.

Instead, the method adopted in the present instrument consists of automatically removing one crystal from the X-ray beam after it has performed a single or a given number of rotations, and replacing the second crystal *in precisely the same position*, which in turn is made to execute the same or a different number of rotations, according to the desired intensity ratio between the two sets of reflexions. The two crystals (C and D, Pl. XV.) are thus alternately exposed to the rays throughout the whole time of the experiment. By this means any variation in the intensity of the X-ray beam during the exposure is averaged out, and so no special control need be kept on the X-ray tube to ensure uniform output. Thus a cold cathode tube can be employed, if desired, which has the advantage of producing a very clean radiation.

In general the apparatus can be used to record the reflexions from any two crystal specimens on one film in one operation. The two sets of reflexions then get identical subsequent treatment as regards development, etc., and accurate comparisons are possible. There are,

therefore, a wide variety of uses for the instrument, such as the correlation of different zones of reflexions, recording the effect on the intensities of heating or cooling one specimen, etc. The outstanding advantage of the present method in such cases is the fact that a whole zone of reflexions from each specimen is recorded in one operation. This is much more important than a few isolated measurements, however accurate, when any really detailed analysis is in view.

The reflexions from the two crystals are sorted out by means of automatic shutters operated by small solenoids (E and F, Pl. XV.), and are recorded side by side on a moving film. Pl. XVI. (*c*) is an example of such a photograph, the reflexions from the second crystal (a small one in this case) being seen to the right of the dotted line.

The use of a moving film for this work has a much more important bearing on the results than mere convenience in identification of the various reflecting planes, although that in itself is a considerable advantage especially in the case of a complex crystal. In recording a weak reflexion on a photographic film or plate the limiting factor is the amount of background due to scattered radiation as compared with the actual intensity of the spot. In the process of measurement this background must be subtracted and, if it is large, the result will be inaccurate. Now in a complete rotation photograph on a stationary film the whole sensitive surface is exposed to the general scattered radiation for the complete 360° of the rotation, while any individual reflexion may occur within a range of 1° or less. Even in an oscillation photograph of say, 15°, it will be seen that the film-surface may be exposed to the scattered radiation many times longer than is actually necessary for recording an individual reflexion. With the moving film, however, the protecting screens (G, Pl. XV.) may be narrowed, so that the film in the neighbourhood of the spot is only exposed to the scattered radiation during the time that the spot is actually being produced by the reflected rays. The background is thus reduced to a minimum. In practice the screens are set wide enough to allow the whole area of the beam reflected from the crystal to pass through, with a small margin to guard against any slight mis-setting of the crystal, which would cause some of the reflexions to depart from the true

equatorial line. A " setting " photograph, of course, is always taken as a check, before or after the moving film exposure, with a stationary film inserted behind the screens.

Several types of moving film camera are in general use *. In this instrument the method adopted is that first used by Robinson, in which the film is mounted on a revolving drum supported by an arm (H, Pl. XV.), which can be set to make any angle with the direction of the X-ray beam. For most purposes this arm may be set so that the film-surface is inclined at an angle of 45° or 60° to the beam, allowing reflexions over a range of θ up to about 55° to be recorded accurately. An interpretation chart and correction factors to allow for the angle of incidence of the reflected beam on the film are given below.

For some purposes the Weissenberg type of moving film camera is preferable. In it the film is mounted inside a cylinder which moves horizontally, and as the reflexions from the equatorial line are always normal to the film-surface, no correction factor is necessary for them. The revolving drum type of camera was adopted for the present instrument to promote greater accessibility to the crystals, and to make the whole instrument more compact. It was also found more convenient to adapt the crystal interchange mechanism to a continuous motion of rotation rather than to the reversing motion necessary with the Weissenberg arrangement. At the same time there is no serious reason why the Weissenberg type of film-holder should not be employed with the present instrument if suitable modifications are made in the rest of the mechanism.

The second object of this spectrometer is to afford a convenient method of making accurate comparisons between very strong and very weak reflexions. This is effected by means of the automatic shutters, which can be set to exclude the strong reflexions for a certain number of rotations of the crystal in a regular sequence throughout the exposure. Two films, showing strong reflexions unreduced, and reduced by a factor of 12, are reproduced in Pl. XVI. (*a*) and (*b*).

* B. W. Robinson, J. Sci. Instr. x. p. 165 (1933) ; Weissenberg, *Zeit. f. Phys.* xxiii. p. 229 (1924) ; Schiebold, *Zeit. f. Kristallog.* lxxxvi. p. 370 (1933).

2. *Details of Mechanism.*

(a) *Crystal Interchange.*—The success of the instrument largely depends upon the crystals being brought into precisely the same position with respect to the X-ray beam every time they are interchanged. The mechanism will be clear from fig. 1. The crystals are mounted on the spindles C and D, which are set $2\frac{1}{4}$ inches apart, this space being provided to accommodate two sets of goniometer arcs. These spindles are driven by the central shaft I,

Fig. 1.
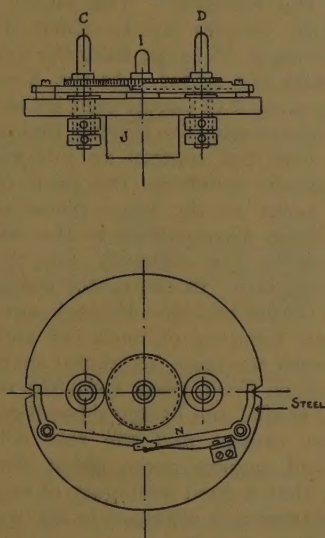
Crystal interchange mechanism.

which is mounted on ball-bearings and takes the drive from the motor through a worm-gear at its base. The circular brass disk, upon which the spindles C and D are mounted, can itself rotate upon an independent set of ball-bearings housed in J. Two V-shaped notches are cut upon the edges of this disk, exactly 180° apart, and when the small roller on the arm K (Pl. XV.) falls into one of these V's the disk is held firmly and accurately in position. But when a current actuates the solenoid L (Pl. XV.) the arm K is pulled back, and at the same

time the toothed lever N engages with the central gear wheel and thus locks the disk to the central shaft, which carries it round until the small roller on K falls into the next V. The crystals have now been interchanged, and continue to rotate about their own axes as before, until a current again actuates the solenoid. The mechanism has a smooth action, and the position of the crystals in the beam is accurate to about 0·1 mm.

(b) *Drive and Gears*.—A small 230 volt A.C. British Thomson-Houston gramophone motor (M, Pl. XV.) is used to drive the machine. This motor runs at constant speed with torques up to about 1200 gm. cm. on the shaft turning at 78 r.p.m. from the worm-reduction gear supplied with the motor. As the X-ray tube may be run from the same A.C. circuit used for the motor, care must be taken, in arranging the gearing, that one revolution of the crystal does not contain an integral number of turns of the motor, otherwise the peak of a reflexion might always occur at the same phase of the X-ray pulse, and so cause discrepancies in the recorded intensities. To overcome this difficulty, and to average out any possible irregularity in the motor gearing, the drive is transmitted to the machine through two gear-wheels containing prime numbers of teeth (41 and 47). These wheels engage with the main horizontal shaft O (Pl. XV.) which by means of worm-gears turns the commutator A and the central shaft I and by spiral bevel gears and chain drive the roller camera and the rear commutator B. The crystals and camera make about five revolutions per minute, so that a good averaging of any fluctuations in the X-ray intensity is obtained in the course of about an hour's exposure.

Special care had to be exercised in cutting the worm-drive and gear wheels leading to the crystal spindles *, as a uniform motion of rotation is essential for accurate results, or at least a motion which is free from periodic irregularities. The rotational motion with the present gearing is found to be sufficiently uniform to give accurate results with most ordinary organic crystals where the reflexions are not extremely sharp. To obtain the most reliable results it is best to employ an X-ray beam with

a divergence of one or more degrees. For increasing the accuracy in dealing with more sharply reflecting crystals, or for use with more nearly parallel X-ray beams, tests are being made with wheels containing a larger number of smaller teeth, and also with helical-cut gearing.

(c) *Camera and Shutters.*—The camera is a hollow brass cylinder 7 inches long and 9 inches in circumference, taking the standard full-plate films ($6\frac{1}{2} \times 8\frac{1}{2}$ inches), with space for protecting cover and clips. A brass plate Q in front carries the adjustable screens and shutters as shown in fig. 2.

Fig. 2.
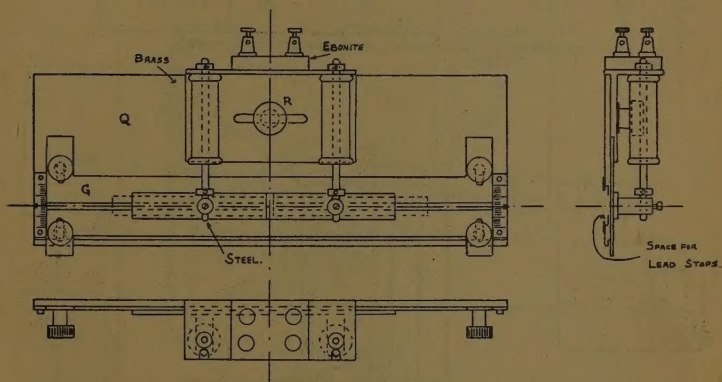
Camera screens and shutters.

A small scale at each end facilitates setting the screens to any desired aperture. The two shutters overlap by $\frac{1}{8}$ inch, and are operated by independent solenoids. They are mounted on a separate plate which can be adjusted to any point along the front of the camera by the screw R. Lead stops for cutting out the direct beam, etc., can be inserted behind and adjusted to any position required by the angular setting of the camera.

(d) *Electrical Connections.*—Commutator A, controlling the crystal interchange, rotates once for every 12 rotations of the crystal and camera, and there is space for 12 easily detachable brass segments on its circumference.

The crystal interchange release only operates when one of these segments closes the circuit, so that by suitably arranging the segments a large number of exposure ratios between the two crystals can be obtained. The exact timing of the release is controlled by a fine adjustment at S (fig. 3).

The current going to the shutter solenoids is sent along either of two leads 11 or 12 by means of the automatic switch at T, depending upon which crystal is rotating

Fig. 3.
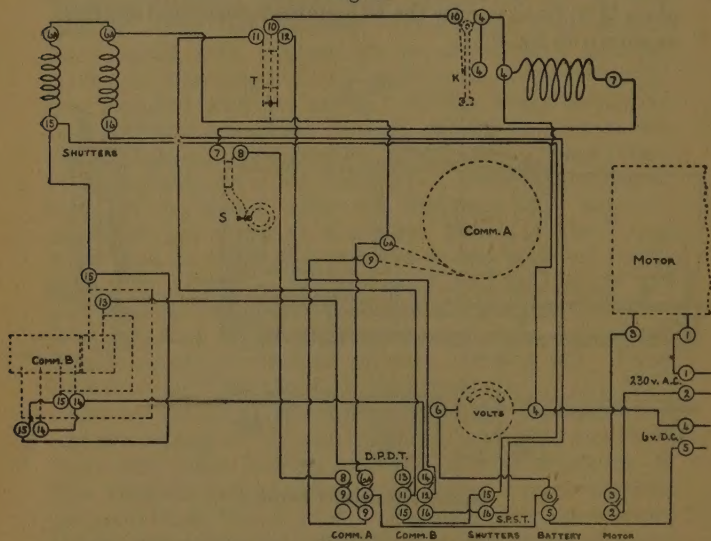
Electrical connexions.

in the X-ray beam. If these leads are connected directly to the shutter solenoids by means of the double-pole double-throw switch marked " Comm. B," then one shutter opens to receive the reflexions from one crystal and the other for the other crystal, so that the reflexions are arranged side by side on the film. This arrangement is very useful for some purposes, especially for correlation, because the strong reflexions of small angle from one crystal are placed side by side with the weak reflexions of large angle from the other crystal.

But when it is desired to record a complete range of reflexions from both crystals, the shutter solenoids are connected in parallel by the switch marked "Shutters," and the leads 11 and 12 are connected to commutator B, the action of which is explained diagramatically in fig. 4. Six brushes on two movable arms are in contact with a rotating disk bearing a semicircle of brass. It will be seen that when the current passes along lead A it is sent to the shutters for $(180° - \theta)$ of the rotation, but when it passes along lead B it is sent to the shutters for the other $(180° + \theta)$ of the rotation. As the shutters act together, the whole width of the moving film for any part of the rotation may thus be reserved for the

Fig. 4.
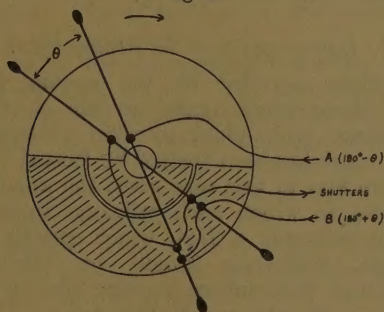
Commutator B.

reflexions of one crystal, and the remainder for the other crystal. Pl. XVI. (c), shows a film taken in this way. In practice it was found convenient to make commutator B in the form of a cylinder which rotates at the same speed as the camera, and is mounted at the rear of the arm carrying the camera (B, Pl. XV.).

In order to prevent any X-rays from reaching the film while the crystals are being interchanged, a cut-out is placed on the crystal interchange release-arm at K, which ensures that both shutters are always closed during the interchange.

A third arrangement of the electrical connexions is made when it is desired to compare strong and weak reflexions from the same crystal. The machine is now used as an ordinary single-crystal spectrometer. The

double-pole double-throw switch marked " Comm. A "
cuts out the crystal interchange release mechanism
entirely, and brings the shutter circuit to commutator A.
The shutters now open only when a brass segment on this
commutator crosses the brushes. Each segment is of
such a size that it keeps the shutters open for one revolu-
tion of the crystal. The shutters are now adjusted on the
camera front until they cover the positions of the reflexions
which it is desired to exclude, and a suitable number of
brass segments are attached to commutator A. If one
segment only is attached, the shutters open for one revo-
lution in twelve, and so the strong reflexions are reduced
twelve times. If two segments are attached, the reduc-
tion factor is $\frac{1}{6}$, and so on. In Pl. XVI. (*b*) the strong
reflexions have been reduced to $\frac{1}{12}$.

3. *Interpretation of the Photographs.*

The reflexions recorded by the moving film roller
camera are those which make up the equatorial line
on an ordinary plane-plate rotation photograph, the
analysis of which has been treated by Bernal [*]. But the
motion of the film in this case gives the angular setting
of the crystal at which each reflexion takes place as
a second coordinate, a fact which greatly aids the
interpretation. Reference should be made to the
interpretation of Weissenberg moving film photographs
given by W. A. Wooster and N. Wooster [†]. The relation
between the Weissenberg moving film photographs and
those taken with the roller camera is simply the relation
between the ordinary circular camera and the plane-plate.

When the roller is set at right angles to the direction
of the incident beam, the distance x of a reflexion of
glancing angle θ from the line which the direct beam makes
on the film is given by

$$x_0 = D \tan 2\theta,$$

where D is the perpendicular distance between the
crystal and the film. But for most purposes it is con-
venient to incline the roller at an angle to the direction
of the beam, in order to record reflexions of large θ.
If ψ is the angle between the normal to the roller and

* Proc. Roy. Soc. A, cxiii. p. 117 (1926).
† *Zeit. für Kristallog.* lxxxiv. p. 327 (1933).

the direction of the X-ray beam, the above relation holds for $\psi = 0°$, and for other settings

$$x = \frac{D \sin 2\theta}{\cos \psi . \cos(\psi - 2\theta)} . \quad \cdots \quad (1)$$

When $\psi = 90°$ the film-surface is parallel to the direct beam, and a new origin must be taken. It is then convenient to measure x_{90} from the line where reflexions having $\theta = 30°$ meet the film, or from $\xi = \lambda/d = 2 \sin \theta = 1 \cdot 000$, in Bernal's notation. Then

$$x_{90} = D (\tan 30° - \cot 2\theta).$$

In Table I. values of x are given for $\psi = 0°$, $30°$, $45°$, $60°$, and $90°$, in terms of ξ, for the crystal at unit distance from the film. These settings of the camera should suffice for all ordinary work.

A chart useful for interpreting the films is given in fig. 5 for the setting $\psi = 60°$. The horizontal coordinate is x, and the vertical coordinate gives the angular setting of the crystal. Similar charts for other settings of the camera can easily be constructed from the table. The vertical lines represent equal increments of ξ, and the curves represent expression (1) repeated at $5°$ intervals. In any photograph the successive orders of any reflexion lie upon these curves. (The scale is arranged for the crystal at $3 \cdot 50$ cm. from the film, and $180°$ is equal to $11 \cdot 48$ cm., half the circumference of the roller camera.) In the corresponding chart for the Weissenberg camera * these curves are straight lines. In the present case they have a point of inflexion at $\xi = 1 \cdot 000$, where the reflected beam is normally incident upon the film.

When the reflected beam strikes the film at an angle it is necessary to apply a correction to the measured intensity to allow for the spreading of the spot and the film absorption. These correction factors have been studied by Cox and Shaw † who give the values of this factor, D_2, for various angles of incidence of the beam upon Doneo films. With the roller camera at the setting ψ, the angle of incidence of the beam on the film is $(\psi - 2\theta)$. Table II. gives the values of D_2 worked out in terms of ξ for various settings of the camera. When

* Compare Wooster, *loc. cit.*
† Proc. Roy. Soc. A, cxxvii. p. 71 (1930).

TABLE I.

Values of $\dfrac{\sin 2\theta}{\cos\psi\,.\,\cos(\psi-2\theta)}$ and of

$(\tan 30° - \cot 2\theta)$ when $\psi = 90°$.

$\lambda/d = 2\sin\theta$	2θ	$\psi = 0°$	$\psi = 30°$	$\psi = 45°$	$\psi = 60°$	$\psi = 90°$
0·050	2° 52′	0·050	0·065	0·095	0·184	−19·39
0·100	5° 44′	0·100	0·127	0·182	0·342	−9·383
0·150	8° 36′	0·151	0·185	0·263	0·479	−6·035
0·200	11° 28′	0·203	0·242	0·337	0·600	−4·352
0·250	14° 22′	0·256	0·297	0·408	0·710	−3·327
0·300	17° 16′	0·311	0·351	0·474	0·808	−2·640
0·350	20° 10′	0·367	0·404	0·537	0·898	−2·146
0·400	23° 4′	0·426	0·456	0·597	0·980	−1·771
0·450	26° 0′	0·488	0·507	0·656	1·057	−1·473
0·500	28° 58′	0·554	0·559	0·713	1·130	−1·229
0·550	31° 56′	0·623	0·611	0·768	1·199	−1·027
0·600	34° 56′	0·698	0·664	0·823	1·265	−0·854
0·650	37° 56′	0·779	0·717	0·876	1·327	−0·706
0·700	40° 58′	0·868	0·771	0·929	1·387	−0·574
0·750	44° 3′	0·967	0·828	0·983	1·446	−0·456
0·800	47° 10′	1·079	0·886	1·037	1·504	−0·350
0·850	50° 18′	1·205	0·947	1·093	1·562	−0·253
0·900	53° 30′	1·351	1·012	1·149	1·618	−0·163
0·950	56° 43′	1·523	1·081	1·208	1·675	−0·079
1·000	60° 0′	1·732	1·155	1·268	1·732	0·000
1·050	63° 20′	1·991	1·235	1·332	1·790	0·075
1·100	66° 44′	2·326	1·324	1·399	1·850	0·147
1·150	70° 12′	2·778	1·422	1·471	1·912	0·217
1·200	73° 44′	3·427	1·534	1·548	1·976	0·286
1·250	77° 22′	4·462	1·664	1·634	2·045	0·353
1·300	81° 6′	6·386	1·816	1·729	2·118	0·421
1·350	84° 54′	11·21	2·000	1·836	2·197	0·488
1·400	88° 51′	49·82	2·231	1·961	2·283	0·557
1·450	92° 56′	. .	2·534	2·108	2·380	0·629
1·500	97° 11′	. .	2·955	2·288	2·491	0·703
1·550	101° 37′	. .	3·586	2·518	2·621	0·783
1·600	106° 16′	. .	4·671	2·824	2·778	0·869
1·650	111° 11′	. .	7·028	3·266	2·975	0·965
1·700	116° 25′	. .	16·56	3·975	3·238	1·074
1·750	122° 6′	. .	. .	5·367	3·620	1·205
1·800	128° 20′	. .	. .	9·559	4·250	1·368
1·850	135° 20′	. .	. .	. .	5·553	1·589
1·900	143° 36′	. .	. .	. .	10·65	1·934
1·950	154° 18′	. .	. .	. .	. .	2·655
2·000	180° 0′	. .	. .	. .	. .	. .

no value is quoted, the correction factor is too large to
be reliable.

Fig. 5.
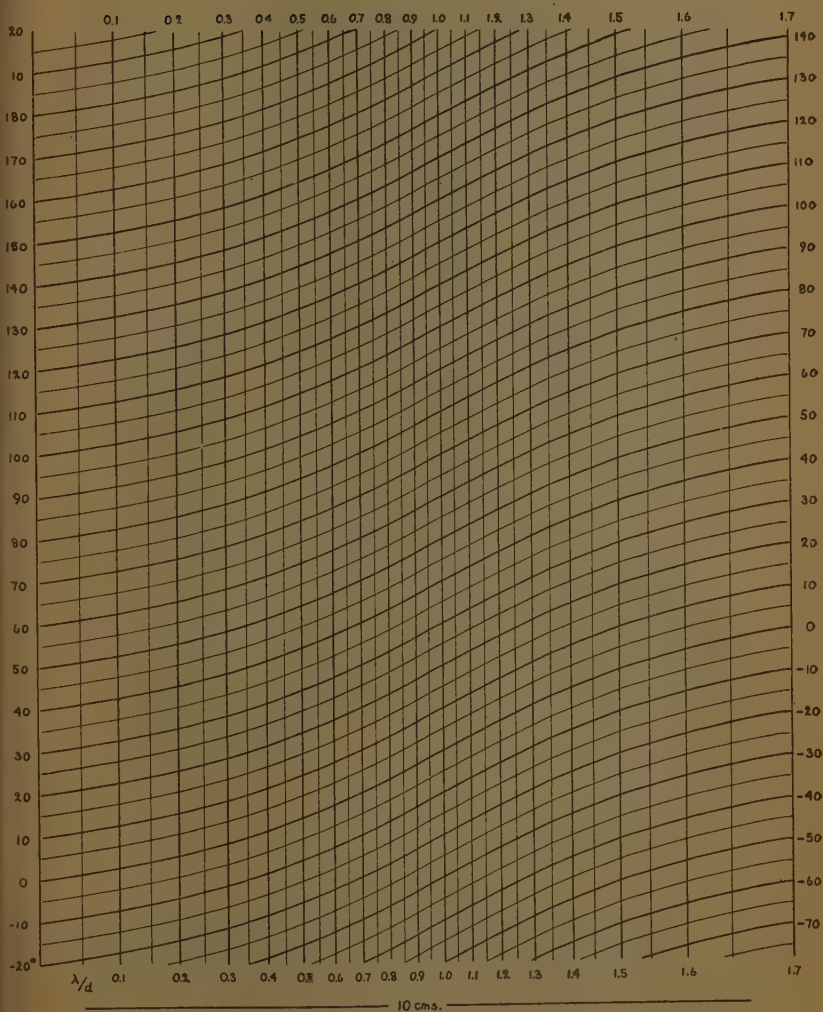
Interpretation chart. $\psi = 60°$, D = 3·50 cm.

Table II.

Values of D_2, the Film Correction Factor.

$\lambda/d = 2\sin\theta$.	$\psi = 0°$.	$\psi = 30°$.	$\psi = 45°$.	$\psi = 60°$.	$\psi = 90°$.
0·050	1·00	0·91	0·79	..	..
0·100	0·995	0·93	0·815	0·66	..
0·150	0·99	0·945	0·84	0·70	..
0·200	0·98	0·955	0·865	0·73	..
0·250	0·975	0·965	0·885	0·76	..
0·300	0·965	0·975	0·905	0·785	..
0·350	0·95	0·985	0·925	0·81	..
0·400	0·935	0·995	0·94	0·84	..
0·450	0·92	1·00	0·955	0·86	..
0·500	0·90	1·00	0·97	0·885	..
0·550	0·875	1·00	0·975	0·905	..
0·600	0·855	0·995	0·985	0·925	0·655
0·650	0·83	0·99	0·995	0·94	0·69
0·700	0·80	0·98	1·00	0·955	0·725
0·750	0·775	0·975	1·00	0·97	0·755
0·800	0·745	0·965	1·00	0·975	0·785
0·850	0·71	0·95	0·995	0·985	0·81
0·900	0·67	0·935	0·99	0·995	0·84
0·950	...	0·915	0·98	1·00	0·865
1·000	..	0·89	0·97	1·00	0·89
1·050	..	0·865	0·96	1·00	0·915
1·100	..	0·84	0·94	0·995	0·935
1·150	..	0·81	0·925	0·985	0·95
1·200	..	0·775	0·90	0·975	0·965
1·250	..	0·74	0·875	0·965	0·975
1·300	..	0·70	0·845	0·945	0·99
1·350	..	0·655	0·81	0·925	0·995
1·400	..	..	0·775	0·90	1·00
1·450	..	..	0·735	0·87	1·00
1·500	..	..	0·69	0·835	0·995
1·550	..	..	..	0·795	0·98
1·600	..	..	..	0·75	0·965
1·650	..	..	..	0·70	0·945
1·700	..	..	..	0·64	0·915
1·750	..	..	..	..	0·875
1·800	..	..	..	..	0·825
1·850	..	..	..	..	0·76
1·900	..	..	..	..	0·67

4. *Results obtained.*

The spectrometer has been in use in the Davy Faraday Laboratory during the past year, being employed chiefly to calibrate X-ray crystal photographs with reflexions of known absolute value, to facilitate comparisons between very strong and very weak reflexions, and for general photographic work. By its use absolute values for the

reflexions of the following organic crystals have been obtained :—Dibenzyl, benzoquinone, resorcinol, dibenanthracene, chrysene, octahydrochrysene, cyanuric triazide, and some of the phthalocyanines. The unstable nature of some of these compounds would render any detailed survey of their intensities on the ionization spectrometer a very difficult task ; and in the case of others only minute crystals can be obtained, which would be too small to give accurate results by the ionization method.

Some figures may be quoted which test the accuracy of the machine. The absolute value of a reflexion from a small crystal of chrysene was measured directly on the ionization spectrometer in monochromatic rays by Dr. Robinson, using a carefully controlled X-ray tube, with the result $F_{002}=75$. With the same chrysene crystal, Dr. Iball employed the two-crystal spectrometer and photographic methods, calibrating the film with five standard reflexions, and using an ordinary cold cathode X-ray tube without special control. He obtained the identical result, $F_{002}=75$. The work was repeated with another chrysene crystal, slightly larger, and the value $F_{002}=72$ was obtained, using the two-crystal spectrometer.

The ratio of the reflecting powers of two crystals of triphenylbenzene was also determined, (*a*) with the ionization spectrometer, in monochromatic rays, using a specially controlled X-ray tube ; and (*b*) with the two-crystal spectrometer and photographic methods, using a small, uncontrolled X-ray tube. The results were (*a*) 2·37, (*b*) 2·34.

		Film				
		1.	2.	3.	4.	5.
Reflexion	A	42·3	41·5	42·5	41·5	41·0
	B	16·8	17·7	19·0	17·4	20·4
	C	20·6	20·8	18·7	20·3	20·8
	D	10·0	9·7	9·3	11·2	8·7
	E	10·3	10·3	10·4	9·7	9·1

It is customary in such work to measure on the photometer about five reflexions from a known standard, recorded near one end of the film (compare Pl. XVI. (*c*)).

The measurements of such a group of five reflexions, taken on different films by different observers, is given below, as showing how far the results can be reproduced. The exposure times vary, of course, but here we are only concerned with relative values, and the figures have been put on a common scale which makes their total equal to 100.

The small variations which occur among these figures might be due to several causes, such as variation in uniformity of the film, unequal exposure to the developer, etc. They are just a little larger than the errors which arise in measuring the films. Further work has made it seem likely, however, that they are chiefly due to small irregularities in the gearing of the machine, because some exposures with more nearly parallel X-ray beams seemed to increase the discrepancies. The more parallel beam has the effect of narrowing the angle over which the reflexion takes place, and so small periodic irregularities in the rotational motion of the crystal would become more important. Recently an improved worm-drive was installed under the main central shaft I, and the latest results seem to be definitely more uniform.

In practice the measurements of about five reflexions of known absolute value are added together, and the combined result is used to place the unknown reflexions from the other crystal on an absolute scale. In this way the effect of any small irregularity is averaged out, and the final result is rendered very reliable.

In conclusion, I am indebted to Sir William Bragg, O.M., F.R.S., and the Managers of the Royal Institution for the facilities afforded at the Davy Faraday Laboratory for carrying out this work. The whole machine was constructed in the laboratory workshops by Mr. Jenkinson, whom I wish to thank for the great care and skill he has bestowed upon it.

Summary.

A two-crystal moving film spectrometer for general use in photographic X-ray crystal analysis is described. The two crystals are alternately exposed to the X-ray beam throughout the whole time of the experiment, thereby averaging out any fluctuations in the output of the X-ray tube, and the reflexions are sorted out and

placed side by side on a moving film of the roller type by means of automatic shutters.

In general the apparatus can be used to record the reflexions from any two crystal specimens on one film in one operation. The two sets of reflexions thus get identical subsequent treatment as regards development, etc., and accurate comparisons are possible. There are a wide variety of uses for the instrument, such as placing the reflexions from an unknown crystal on an absolute scale by comparison with those of an accurately known standard, recording the effect on the intensities of heating or cooling one specimen, etc. The fact that a whole zone of reflexions from each crystal can be recorded in one operation makes the present method important when any really detailed analysis is in view.

When used with a single crystal in ordinary work, the automatic shutters can be employed to reduce the strong reflexions by a given factor, and so render their comparison with the weaker reflexions more accurate.

Tables of constants and correction factors have been computed, and a chart prepared, to aid the interpretation of the films.

Examples of results obtained are given.

Davy Faraday Laboratory,
 The Royal Institution.
  11th June, 1934.

LXXI. *Considerations on Micro-calorimetry.* By Brian Whipp, *Ph.D.* [*]

MICRO-CALORIMETRY should become increasingly important in the study of many reaction systems, because it permits the use of small quantities or concentrations of reactants, so that conditions are kept as simple as possible. It is, therefore, of interest to inquire into the maximum sensitivity of a measuring instrument suitable for general purposes.

In the course of work on the adsorption of vapours on solid surfaces, the writer wished to measure heats of adsorption of the order of 10^{-4} to 10^{-3} calorie. A

calorimeter was required which would detect 10^{-6} calorie. No description of a sufficiently sensitive instrument was to be found in the published literature. Moreover, existing calorimeters were so complicated that success appeared to depend upon the introduction of some new principle in the design *.

As a result of analysis of the thermo-electric circuit involved, it has been found possible greatly to simplify the design for measurements of heats of adsorption, while obtaining the desired activity. It has appeared useful to record the results, as their application seemed of wider interest in physical and biological work.

The chief advance made as a result of the analysis has been the use of a small number (ca. 5) of thermocouples and a low-circuit resistance (ca. 2 ohms) instead of the large number of thermo couples and high resistance generally favoured by previous workers. A complicated thermostat has been avoided by symmetrical construction and use of the differential principle.

The use of a small number of couples made it possible to devote more attention to the design of the individual thermo-junctions, whereby many improvements have been effected. Intimate contact between the junctions and the calorimeter vessel is assured and, as no organic insulating material is required, the junctions may easily be dismantled and will withstand high temperatures.

It is assumed that the heat capacity of the system in which the heat is evolved is fairly large compared with that of the couples—in particular that a container is required for the reactants.

The differential method is generally best adapted for the measurement of sudden heat effects. Two identical calorimeters, one of which is simply a dummy, are symmetrically arranged with respect to the axis inside a cylindrical container which provides a uniform temperature environment. Their difference of temperature following upon the evolution of heat in one of them is

* Among earlier work may be noted that of Lange—for references see Lang and Robinson, Chem. Review, ix. no. 1, p. 89 (1931); Ellis & Wooster, Proc. Roy. Soc. A, cxvii. p. 109 (1927); A. V. Hill, Proc. Roy. Soc. B, cxi. p. 106 (1932), etc.; Tian, *C. R.* clxxviii. p. 705 (1924); *cf.* also Berenger-Calvet, *J. Chim. Phys.* xxiv. p. 325 (1927); Ward, Proc. Camb. Phil. Soc. xxvi. p. 278 (1930); and Moll and Burger, *Zeit. für Physik*, xxxii. p. 575 (1925). This work will not be discussed further here.

measured. The temperature of the environment need not be constant provided that it is symmetrically uniform with regard to the axis of the container.

A separate advantage of the dummy calorimeter is that it enables us to compensate for undesirable subsidiary heat effects accompanying the heat which is to be measured. The subsidiary effects are simultaneously produced in the dummy, so that the temperature difference recorded corresponds only to the heat which it is desired to measure.

An example of such a subsidiary effect is to be found in the heat of compression of a gas (*cf.* Ward, Proc. Roy. Soc. A, cxxxiii. p. 511, 1931). This heat is evolved whenever the pressure of gas inside a vessel is changed. Thus, a change of pressure of 2 mm. in a vessel of 10 c.c. capacity produces $1\cdot7 \times 10^{-3}$ calorie, which may be larger than a heat of adsorption to be measured. The effect may be compensated by arranging for an equal change of pressure in the dummy.

An analysis of the action of a differential calorimeter, when heat is evolved in the dummy as well as in the real calorimeter, will be given.

If it is required to measure a steady, long-continued heat evolution, the best plan is to measure the equilibrium temperature difference finally attained, as in the work of Ellis and Wooster (*loc. cit.*).

When a variable heat evolution is to be measured over a long period, the heat loss becomes more important, and it is convenient to make it small by partial compensation by Peltier cooling (*cf.* Berenger-Calvet (*loc. cit.*) and Ward (*loc. cit.*). In their arrangements a large number of Peltier junctions was employed, the object being to reduce the Joule heating by the use of small currents. But there seems to be no reason why a small number of Peltier junctions should not have sufficed, provided that their resistance had been made small. Thus the advantages of using a small number of couples need not be lost.

The Maximum Sensitivity of a Galvanometer and Thermo-couples.

Multiplication of the number of couples only results in increased sensitivity when their E.M.F. is read on open circuit, as, for example, by a potentiometer. Poten-

tiometers introduce parasitic E.M.F.s of the order of 10^{-7} volt under the most favourable conditions (White, J. A. C. S. xxxvi. p. 1858 (1914)), and calculation shows that their use is not generally practicable when a sensitivity of 10^{-6} ° C. is required. When a galvanometer is used directly across the couples, current will flow from them, but this will be limited by the total resistance in circuit.

Suppose we have n couples in series and connected across a galvanometer of resistance G ohms. Let r be the resistance of each couple, and let e volts be its E.M.F. per ° C. difference in the temperature of the junctions. Then the current through the galvanometer is

$$i = \frac{ne}{nr + G} \text{ ampere} \quad . \quad . \quad . \quad . \quad (1)$$

Suppose θ is the deflexion of the galvanometer for this current. Now for galvanometers the coils of which are wound in similar channels, and contain the same mass of wire, the current sensitivity varies approximately as the square root of the resistance of the coil (Glazebrook, ' Dictionary of Applied Physics,' vol. ii. pp. 366–7). We may therefore write,

$$\theta = ki\sqrt{G},$$

where k is a constant for such a galvanometer. This expression will hold equally well for galvanometers of the moving-magnet and moving-coil types.

Thus, from (1),

$$\theta = \frac{kne\sqrt{G}}{nr + G} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In order that θ may be large, n should be large and r should be small. It will be shown later (see equation 7), that the ratio n/r cannot be allowed to increase beyond a certain limit h, dependent upon the maximum permissible rate of heat loss per degree temperature excess from hot to cold junctions through the wires of the couples. Under these conditions we may show that θ is a maximum when $nr = G$.

With this requirement satisfied, equation (2) becomes

$$\theta = \frac{ke}{2} \sqrt{\frac{n}{r}} = \frac{ke}{2} \sqrt{h}. \quad . \quad . \quad . \quad (3)$$

Let k_1 and k_2 be the thermal conductivities, ρ_1 and ρ_2 the specific resistances and a_1 and a_2 the areas of cross-section of the two wires in each couple, and l their length. Then

$$H = n \frac{(k_1 a_1 + k_2 a_2)}{l}.$$

Now for the minimum ratio, $\dfrac{\text{heat loss}}{\text{electrical conductivity}}$, of a couple, it may be shown that

$$a_2/a_1 = \sqrt{\frac{k_1 \rho_2}{k_2 \rho_1}} \quad . \quad . \quad . \quad . \quad (4)$$

If the two wires of the couples are chosen so as to conform to this requirement,

$$H = \frac{n a_1}{l} \left\{ k_1 + \sqrt{\frac{k_1 k_2 \rho_2}{\rho_1}} \right\}.$$

Since $\qquad r = l(\rho_1/a_1 + \rho_0/a_2),$

we obtain from (4),

$$h = n/r = \frac{n a_1}{l \left\{ \rho_1 + \sqrt{\dfrac{\rho_1 \rho_2 k_2}{k_1}} \right\}};$$

$\therefore$ from (5)

$$h = \frac{H}{\{\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}\}^2}. \quad . \quad . \quad . \quad (7)$$

(This equation shows that the value of h, i. e., n/r, is limited by H, and as $k\rho$ is constant (see later), the limiting value is independent of the type of couple used.)

Substituting for h in (3), we obtain for the maximum value of θ the temperature sensitivity of the arrangement:

$$\theta_{\text{max.}} = \frac{k e \sqrt{H}}{2\{\sqrt{k_1 \rho_1} + \sqrt{k_2 \rho_2}\}}. \quad . \quad . \quad . \quad (8)$$

As $k\rho$ for all metals and alloys is approximately constant (law of Wiedemann and Franz), $\theta_{\text{max.}}$ depends simply on (1) the current sensitivity of the galvanometer divided by the square root of its resistance, (2) the thermoelectric power of the type of couple used, and (3) the square root of the maximum permissible heat loss.

When discrete amounts of heat are suddenly evolved, the steady state will not be reached, and the initial heat loss will be greater than that calculated from equation (5). In this case empirical work on the best size of wires would help to increase the sensitivity slightly, but this has not been judged worth while in the author's case.

Provided that parasitic E.M.F.s can be eliminated, the smaller the resistance of the galvanometer and couples the simpler the experimental arrangement will be. The Paschen galvanometer gives the largest ratio for $\dfrac{\text{current sensitivity}}{\sqrt{\text{resistance}}}$, and it has the further advantage that the damping is mechanically adjustable and not markedly dependent on the resistance in circuit. The resistance of such a galvanometer may be made very small by connecting the coils in parallel, so that few couples are required.

Having decided how large H may be made, we may calculate h, that is, n/r. The actual values of n and r may now be found by putting $nr = G$.

Example.—Copper-constantan couples were used for two reasons :—(1) To eliminate the magnetic effects found when iron-constantan couples were used ; (2) to eliminate thermo-electric potentials at the junctions of the copper leads and the thermo-couples.

By calculation from equation (4) we find the optimum ratio of cross-section for the constantan and copper wires to be 22. Equating nr to the galvanometer resistance (0·75 ohm) and n/r to h (calculated from (7), taking H as 5×10^{-4} cal./° C./sec.), we find $n = 6$ and $r = 0·125$ ohm.

The distance from hot to cold junctions being 7 cm., we now calculate the diameters of the wires, and find that 36 S.W.G. copper and 22 S.W.G. constantan are required.

In order to give a more quantitative idea of the improvements made, the available thermal and electrical data of three other calorimeters are given along with those of the author's in Table I. Most of the figures are very approximate.

It should be mentioned that Hill has not been so much concerned with the maximum heat sensitivity of his apparatus as with the analysis of the time-course of the evolution of heat, using an extremely small time interval.

The high heat sensitivity of his apparatus is due to the large number and very low resistance of his couples, but it is doubtful whether his apparatus could be modified to work as an ordinary calorimeter, while preserving this sensitivity, because of the high heat loss through the couples.

In the author's case the calculated sensitivities are given. The observed heat sensitivity was equal to the calculated within a few per cent. when allowance had been made for variations of the galvanometer sensitivity.

TABLE I.

	Ward.	Hill.	Lange.	Author.
Water-equivalent of heat system (grms.) .	50	0·6 (calc.)	1000	1
No. of couples	31	150	$c.$ 1100	5
Temperature sensitivity (°C./mm.)	4×10^{-5}	10^{-6}	0.6×10^{-6}	3×10^{-6}
Heat sensitivity (cal./mm.)	2×10^{-3}	0.5×10^{-6}	0.6×10^{-3}	3×10^{-6}
Resistance of couples (ohms)	11·5	50	75	1
Resistance of galvanometer (ohms)	8·5	25	25	1
Sensitivity of galvanometer (amp./mm.)..	3.5×10^{-9}	3.3×10^{-10}	10^{-9}	3×10^{-10}
Insulation of couples ..	organic	organic	organic	glass
R_1	6.2×10^{-2}	7.5×10^{-5}	0·6	1.5×10^{-5}
F_1 (relative values)....	4	240	1	1120

R_1 is the " heat sensitivity for one couple," *i. e.*, the heat sensitivity in cal./mm. *multiplied* by the number of couples.

F_1 may be called the sensitivity factor of the calorimeter per couple. It is the galvanometer sensitivity divided by R_1. The larger F_1 the more sensitive each couple becomes.

The Differential System.

The calorimeter proper, B and its dummy B′, are symmetrically arranged with respect to the central vertical axis (shown dotted in fig. 2) of a container of as uniform temperature as possible. B and B′ are as nearly as possible identical, so that, if the temperature of the container varies, it will affect both of them equally. It is only necessary that the temperature inside the container

should be the same at any instant at equal distances from the central axis, and to that end the container (in the writer's case) was made of thick copper in the form of a cylinder and was packed in cotton-wool inside a large Dewar vessel.

The temperature recorded is the difference between the temperatures of the outside surfaces of B and B'. (It is an advantage to deal with surface rather than

Fig. 1.
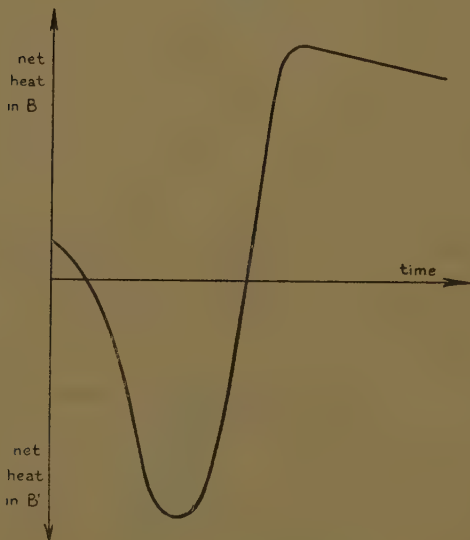
internal temperatures, since it is the former which determine heat losses.)

Suppose now that heat is evolved in B and B' simultaneously, and we desire to measure the net heat evolved in B. It may well be that the heat liberated in B' reaches the cold junctions (i. e., those round the dummy B') before that in B reaches the hot junctions, so that the resulting deflexion-time curve of the galvanometer may be of the form shown in fig. 1. It is important to know how to make the cooling correction in such a case.

Analysis.

Let the temperature of the calorimeter vessel be T, and that of the dummy T′ at a time t after the evolution of different amounts of heat in them. Let T_0 and $T_0{}'$ be their respective temperatures initially. Let T_c be the temperature of the container. Let h and h' be the rates of heat liberation on hot- and cold-junction systems from the calorimeter and dummy vessels following upon, say, the introduction of gas, and let H_t and $H_t{}'$ be the total heats received by the hot and cold junctions respectively up to time t. Let C and C′ be the heat capacities * of the thermo-junction systems. The thermo-couples measure the temperature difference $(T-T')$, which we shall call θ. Then if k and k' are the temperature-cooling coefficients of the calorimeter vessel and dummy, so that for normal cooling of either we have

$$\frac{d(T-T_c)}{dt} = -k(T-T_c),$$

and if k_t be a constant, determining the heat loss through the thermo-couple wires, we have, at time t,

$$\frac{d\theta}{dt} = \frac{d(T-T')}{dt} = \frac{dT}{dt} - \frac{dT'}{dt} = \left\{ \frac{h}{c} - k(T-T_c) \right\}$$
$$- \left\{ \frac{h'}{c'} - k'(T'-T_c) \right\} - 2k_t(T-T').$$

Integrating between $t=0$ and $t=t$,

$$\theta - \theta_0 = \int_0^t \left(\frac{h}{c} - \frac{h'}{c'} \right) dt$$
$$- \int_0^t \left\{ k(T-T_c) - k'(T'-T_c) \right\} dt - 2k_t \int_0^t \theta \,.\, dt,$$

where θ_0 is the initial temperature difference between the couples.

If $k = k'$,

$$\theta - \theta_0 = \int_0^t \left(\frac{h}{c} - \frac{h'}{c'} \right) dt - k \int_0^t \theta \,.\, dt - 2k_t \int_0^t \theta \,.\, dt$$
$$= \left(\frac{H_t}{c} - \frac{H_t{}'}{c'} \right) - (k + 2k_t) \int_0^t \theta \,.\, dt.$$

Only in this case does the term in T_c disappear.

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* These were large compared with the heat capacities of the thermo-couple wires.

The second term is the cooling correction which may be applied, in the Newtonian way, to the galvanometer deflexion.

After a certain time practically no more heat will be received from inside the vessels by either junction system. After this state has been reached the first integral remains constant, so that, differentiating,

$$\frac{d\theta}{dt} = -(k+2k_l)\theta = \text{(say) } k_0\theta.$$

Thus, when temperature equilibrium has been established between the two vessels and their thermo-junction systems, the variation of the galvanometer deflexion obeys the Newtonian law.

If the shape of the deflexion-time curve is complex, it is necessary to compute the area beneath the curve to determine the heat loss.

The disadvantages of the differential calorimeter arise from the difficulty of making the two calorimeters identical in all respects. Unless this is done the above analysis will not apply accurately. Apart from balancing of size, heat capacity, etc., the cooling coefficients k, k' should be the same. The adjustment may be made, if necessary, by partial blackening of one calorimeter.

The balancing of heat capacities of the two calorimeters may best be done by having a small heater (see later) in each of them, and adding inert material to one until the same galvanometer response is obtained for the liberation of equal amounts of heat in each of them. Thick copper wire is useful for this purpose, owing to its high heat conductivity. In experiments involving the introduction of gas, glass beads may be added to adjust the volumes until the same heats of compression are obtained, using an inert gas. In practice the two calorimeters may never be at the same temperature. It is therefore necessary to find indirectly the reading of the galvanometer which corresponds to zero-temperature difference. This may be done by commutating the current from the thermo-couples and taking the mean of the galvanometer deflexions. Alternatively, it may be found by calculation from the observed rates of cooling at two widely different temperature differences as follows.

Suppose x denotes readings of the galvanometer,

and let x_0 be the reading for temperature equality of the two calorimeters.

Then $$x - x_0 = \theta.$$

But we know that

$$\frac{d\theta}{dt} = -k_0\theta,$$

and, therefore,

$$\frac{d(x - x_0)}{dt} = \frac{dx}{dt} = -k_0(x - x_0).$$

If we now substitute the two observed values of $\frac{dx}{dt}$ and x we may solve simultaneously for k_0 and the zero deflexion x_0.

The Single Calorimeter.

Here the temperature difference between the calorimeter and its environment must be measured to estimate the cooling correction, and it is important that the temperature of the environment should remain constant within closer limits than the desired temperature sensitivity of the arrangement. For this purpose Tian and Ward (*loc. cit.*) have used the multiple-wall thermostat of Tian which, in Ward's case, maintained temperatures constant to 2×10^{-6} ° C.

This arrangement is probably ideal for the study of long-continued heat evolutions, particularly where the required temperature sensitivity is not too high (say 10^{-4} ° C.). A small number of thermo-couples may be used on the plan given above, and no balancing of heat losses, capacities, etc., is required, as in the differential method. On the other hand, subsidiary sources of heat cannot be automatically separated from those which it is desired to measure, and a long time (in some cases days) is necessary for the attainment of thermal equilibrium in the thermostat unless special methods are used to hasten it.

Neutralization of the heat evolved over long periods by Peltier cooling may be used, the cooling junctions being arranged in the calorimeter and the heating junctions in the thermostat. No complications due to temperature uncertainties of the latter are then introduced.

Calibration.

It is generally inadvisable to calculate the heat by conversion of galvanometer readings into calories from the heat capacity of the system, the thermo-electric power of the couples, the sensitivity of the galvanometer, and the circuit resistance. A state of affairs far nearer to the theoretical ideal than is practically possible is thereby assumed.

The only reliable general method is to liberate quantities of heat under conditions which are as nearly as possible identical with those of a normal experiment and to calibrate the galvanometer deflexions (corrected for cooling loss) directly in terms of units of heat.

The writer has found electrical calibration by means of resistances made of fine platinum (wound on and enclosed by fine-drawn glass capillary) useful for this purpose. (The change of resistance due to the heating by the current used in calibration was always less than 1 per cent. of the total.) Such resistances of 50 ohms may be easily enclosed in a capillary glass tube 50 mm. long and 1 mm. diameter. Provided that the resistance is surrounded by gas or liquid, the heat may be fairly uniformly spread over the entire contents of the calorimeter. The resistance may also be used as a platinum thermometer, if it is required, to bake the contents of the calorimeter.

Some typical results of calibrations made by the writer are given in the following table. The same heating

Table II.

Experiment.	26 a.	26 b.	26 c.	26 d.	Mean deflexion.	Sensitivity in cal./mm. deflexion.
10^{-3} cal.	—	—	30·2	30·1	30·15	$3·3 \times 10^{-6}$
5×10^{-4} cal. ..	16·5	15·6	—	—	16·0	$3·14 \times 10^{-6}$

current, was used and was passed for 30 seconds in the 10^{-3} calorie calibrations and 15 seconds in the 5×10^{-4} calorie calibrations. The results given are corrected galvanometer deflexions in centimetres.

In these experiments the calibrating resistance was hung inside the calorimeter vessel, which contained hydrogen gas to a pressure of about 5 mm.

General Practical Details.

1. *The Thermo-electric Circuit.*

As the resistance of the galvanometer and thermo-couples is only 2 ohms, special precautions have to be taken to eliminate parasitic E.M.F.s. These may arise from stray thermo-electric effects (as, for example, at the galvanometer terminals), from effects of magnetic induction, and from electrical leaks into the circuit.

To avoid thermo-electric effects the wires from the calorimeter to galvanometer should be of untinned copper throughout, and there should be no soldered joints outside the calorimeter. The Paschen galvano-meter should have copper terminals. If a commutating key is used between the calorimeter and galvanometer it should be entirely of copper (four large copper quadrants with large copper plugs were used by the writer), and the wires to the copper terminals should be wrapped round the terminal a number of times as recommended by White (J. A. C. S. xxxvi. p. 1863 (1914)), so that there is no temperature gradient at the junction of the end of the wire and the terminal. The key and the galvanometer terminals must be well lagged with cotton-wool. Careful attention must be paid to insulation (see, for example, White, J. A. C. S. xxxvi. p. 2011 (1914)). In order to reduce effects due to the variation of magnetic fields in the vicinity (*e. g.*, the field produced by changing the current through a rheostat), the connecting wires should be twisted together to make the circuit as non-inductive as possible.

2. *The Thermo-couples.*

Each thermo-junction was bolted to a silver strap which tightly encircled the calorimeter vessel or its dummy. These latter were made of thin glass in order to transmit the heat as quickly as possible. Small gaps between the silver straps served to insulate the junctions from one another (fig. 2 (*a*)).

The type of junction developed is shown in ·fig. 2 (*b*). The constantan and copper wires (*a* and *b* respectively), are silver-soldered to a small right-angled bracket X

made of silver-foil of thickness 0·1 mm. Two holes
in the other face of the bracket are used to bolt it between
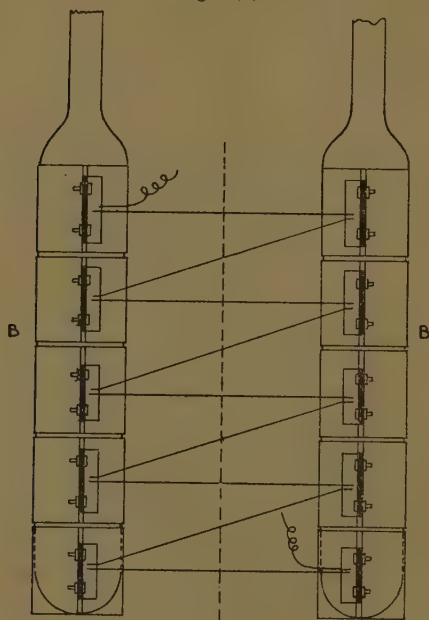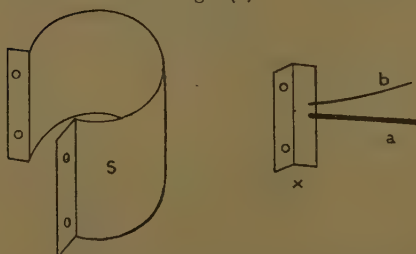
Fig. 2 (*a*).

Fig. 2 (*b*).

the ends of the silver-foil strap S, which tightens round
the calorimeter vessel or dummy by the action of the
bolts. These bolts have washers at each end. The strap
is of the same thickness of foil as the bracket.

Thus the maximum amount of heat is conducted to the thermo-junctions and the couples are readily detachable. If the outside container is evacuated or filled with nitrogen to prevent oxidation of the silver, the whole calorimeter may be baked at a high temperature with all the parts *in situ*. The silver straps being on the outside of the calorimeter vessel and dummy, they decrease the radiation loss, and the temperature difference which is measured is that between the outside of each vessel. It is this temperature difference which determines the heat-loss correction.

Steadiness.

The differential apparatus actually used was almost always thermally steady, there being little drift of the galvanometer spot. No attempt was made to thermostat the apparatus or to shield it from draughts or Bunsen flames in the cellar in which the experiments were carried out. On some days there was a fairly large difference of temperature between the hot and cold junctions, and then the galvanometer drift had to be taken into account. This shows that a thicker copper container or a thermostat would be an advantage, at least where lengthy experiments are concerned (*cf.* Ellis and Wooster, *loc. cit.*, who used a very thick well-lagged copper block to contain their calorimeter).

Summary.

A discussion is given of a method of general microcalorimetry of greatly increased sensitivity.

LXXII. *Note on the Divergent Flow of Fluid.*
By W. R. DEAN, M.A., *Trinity College, Cambridge* *.

1. THE present paper contains a part of some work lately undertaken to examine the stability of the divergent flow of fluid. Such flow is, as is well known, found in practice to be highly unstable, and it therefore

seemed possible that it could be proved to be unstable
in some cases for small disturbances. As a preliminary,
some steady motions slightly different from divergent
radial flow are considered in this paper, since some
previous instances show that such solutions can provide
evidence of instability.

The problem of the two-dimensional radial flow of vis-
cous liquid appears to have been first solved by G. Hamel.
Hamel showed also that there are special steady motions
slightly different from radial flow ; solutions of the same
type are considered in this paper, and their bearing on
the stability of the radial motion is discussed.   The
method of this paper is fairly general, but in the numerical
work illustrating it a special type of divergent flow is
considered, with the result that some of the solutions
are the same as some previously obtained by Hamel ;
the other solutions obtained for the special type of di-
vergent flow appear to be new.

2. Referred to cylindrical coordinates (r, θ, z), the
equations for steady two-dimensional motion of in-
compressible fluid are

$$u \frac{\partial u}{\partial r} + \frac{v}{r} \frac{\partial u}{\partial \theta} - \frac{v^2}{r}$$

$$= -\frac{\partial}{\partial r}\left(\frac{p}{\rho}\right) + v\left(\frac{\partial^2 u}{\partial r^2} + \frac{1}{r} \frac{\partial u}{\partial r} + \frac{1}{r^2} \frac{\partial^2 u}{\partial \theta^2} - \frac{u}{r^2} - \frac{2}{r^2} \frac{\partial v}{\partial \theta}\right), \quad (1)$$

$$u \frac{\partial v}{\partial r} + \frac{v}{r} \frac{\partial v}{\partial \theta} + \frac{uv}{r}$$

$$= -\frac{1}{r} \frac{\partial}{\partial \theta}\left(\frac{p}{\rho}\right) + v\left(\frac{\partial^2 v}{\partial r^2} + \frac{1}{r} \frac{\partial v}{\partial r} + \frac{1}{r^2} \frac{\partial^2 v}{\partial \theta^2} - \frac{v}{r^2} + \frac{2}{r^2} \frac{\partial u}{\partial \theta}\right), \quad (2)$$

and

$$\frac{\partial u}{\partial r} + \frac{u}{r} + \frac{1}{r} \frac{\partial v}{\partial \theta} = 0, \quad . \quad . \quad . \quad . \quad (3)$$

where p is the pressure, ρ the density, and ν the kinematic
coefficient of viscosity ; it is assumed that u, v and p
are independent of z, and that the z component of the
velocity vanishes. In the case of purely radial motion
$(v=0)$ these equations have been solved by G. Hamel *.

* *Jahresb. d. deutschen Math. Ver.* xxv. pp. 34–60 (1917).

In this case the equation of continuity (3) can be written

$$\frac{\partial}{\partial r}(ru)=0,$$

so that

$$u=U/r, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where U is a function of θ only. Equations (1) and (2) become

$$\frac{\partial}{\partial r}\left(\frac{p}{\rho}\right)=\frac{1}{r^3}(\nu U''+U^2),$$

$$\frac{\partial}{\partial \theta}\left(\frac{p}{\rho}\right)=\frac{2\nu}{r^2}U',$$

where accents denote differentiations with respect to θ; eliminating p/ρ, we have

$$U'''+4U'=-\frac{2}{\nu}UU',$$

whence

$$U'^2=\frac{2}{3\nu}(e_1-U)(e_2-U)(e_3-U), \quad . \quad . \quad . \quad (5)$$

e_1, e_2, and e_3 being constants such that

$$e_1+e_2+e_3=-6\nu. \quad . \quad . \quad . \quad . \quad (6)$$

It is now assumed that e_1, e_2, and e_3 are real; since in the general case (which is examined by Hamel) two of the constants may be complex, the following discussion is therefore restricted to a special type of radial motion. The constants being supposed real, we can assume, without further loss of generality, that

$$e_1 \geq e_2 \geq e_3. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If we now write

$$U=e_1\cos^2\psi+e_2\sin^2\psi, \quad . \quad . \quad . \quad . \quad (8)$$

equation (5) becomes

$$\left(\frac{d\psi}{d\theta}\right)^2=\frac{e_1-e_3}{6\nu}(1-k^2\sin^2\psi), \quad . \quad . \quad (9)$$

where

$$k^2=\frac{e_1-e_2}{e_1-e_3}, \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and, if $\theta = 0$ when $\psi = 0$,

$$U = e_1 - (e_1 - e_2) \operatorname{sn}^2 \left[\left(\frac{e_1 - e_3}{6\nu} \right)^{1/2} \theta \right]. \quad . \quad . \quad (11)$$

3. In what follows only the special case in which $e_2 = 0$ is considered. It is not necessary to impose in this way a further restriction on the type of radial motion, since the method employed below evidently applies whatever the real value of e_2; but, besides simplifying the work to some extent, the special case is of interest in itself, and provides a sufficient illustration of the method. If then $e_2 = 0$,

$$U = e_1 \operatorname{cn}^2 \left[\left(\frac{e_1 - e_3}{6\nu} \right)^{1/2} \theta \right], \quad . \quad . \quad . \quad (12)$$

$$k^2 = \frac{e_1}{e_1 - e_3}, \quad . \quad . \quad . \quad . \quad (13)$$

and

$$e_1 + e_3 = -6\nu. \quad . \quad . \quad . \quad . \quad (14)$$

The assumption $e_2 = 0$, taken together with (7), implies that $e_1 \geq 0$; the radial motion is therefore divergent. The maximum value of U is e_1, while U, and therefore u, vanishes when $\theta = \pm \alpha$, α being given by

$$\left(\frac{e_1 - e_3}{6\nu} \right)^{1/2} \alpha = \mathrm{K} = \int_0^{\pi/2} (1 - k^2 \sin^2 \psi)^{-1/2} d\psi.$$

The motion has been examined in detail for a range of values of e_1 from ν to 8ν; the following table shows the corresponding values of α, k^2, K, and also of E, defined by

$$\mathrm{E} = \int_0^{\pi/2} (1 - k^2 \sin^2 \psi)^{1/2} d\psi.$$

e_1	ν	2ν	4ν	8ν
k^2	0·1250	0·2000	0·2857	0·3636
$2\alpha/\pi$	0·8952	0·8184	0·7108	0·5828
$2\mathrm{K}/\pi$	1·0337	1·0565	1·0858	1·1161
$2\mathrm{E}/\pi$	0·9680	0·9479	0·9242	0·9017

It will be seen that as e_1, and, therefore, the maximum radial velocity at given distance from the opening of the

channel, increases, the angle 2α between the walls of the channel decreases.

4. Consider now a steady two-dimensional motion which is slightly different from purely radial motion; substitute in equations (1) to (3) first, as above,

$$u = U/r, \quad v = 0,$$

then

$$u = U/r + u', \quad v = v', \qquad . \quad . \quad . \quad (15)$$

and subtract the two sets of equations, denoting by p' the difference between the two pressures. If u', v', and p' are assumed to be functions of r and θ only, and if squares and products of these quantities are ignored, we reach the equations

$$U\left(\frac{1}{r}\frac{\partial u'}{\partial r} - \frac{u'}{r^2}\right) + U'\frac{v'}{r^2}$$

$$= -\frac{\partial}{\partial r}\left(\frac{p'}{\rho}\right) + \nu\left(\frac{\partial^2 u'}{\partial r^2} + \frac{1}{r}\frac{\partial u'}{\partial r} + \frac{1}{r^2}\frac{\partial^2 u'}{\partial \theta^2} - \frac{u'}{r^2} - \frac{2}{r^2}\frac{\partial v'}{\partial \theta}\right),$$

$$U\left(\frac{1}{r}\frac{\partial v'}{\partial r} + \frac{v'}{r^2}\right)$$

$$= -\frac{1}{r}\frac{\partial}{\partial \theta}\left(\frac{p'}{\rho}\right) + \nu\left(\frac{\partial^2 v'}{\partial r^2} + \frac{1}{r}\frac{\partial v'}{\partial r} + \frac{1}{r^2}\frac{\partial^2 v'}{\partial \theta^2} - \frac{v'}{r^2} + \frac{2}{r^2}\frac{\partial u'}{\partial \theta}\right),$$

and

$$\frac{\partial u'}{\partial r} + \frac{u'}{r} + \frac{1}{r}\frac{\partial v'}{\partial \theta} = 0.$$

These equations are satisfied by the substitutions

$$u' = u_1 r^n, \quad v' = v_1 r^n, \quad p'/\rho = p_1 r^{n-1}, \qquad . \quad . \quad (16)$$

where n is a constant and u_1, v_1, and p_1 are functions of θ only, provided that

$$U(n-1)u_1 + U'v_1$$

$$= -(n-1)p_1 + \nu\left[\frac{d^2u_1}{d\theta^2} + (n^2-1)u_1 - 2\frac{dv_1}{d\theta}\right], \quad (17)$$

$$U(n+1)v_1$$

$$= -\frac{dp_1}{d\theta} + \nu\left[\frac{d^2v_1}{d\theta^2} + (n^2-1)v_1 + 2\frac{du_1}{d\theta}\right], \quad . \quad . \quad (18)$$

and

$$\frac{dv_1}{d\theta} + (n+1)u_1 = 0. \quad . \quad . \quad . \quad . \quad (19)$$

Eliminating p_1 from (17) and (18) and using (19), we have

$$\left[\frac{d^2}{d\theta^2} + (n+1)^2 \right] \left[\frac{du_1}{d\theta} - \frac{(n-1)^2}{n+1} v_1 \right]$$

$$= \frac{1}{\nu} \left[U'' v_1 - 2U' u_1 + (n-1)U \left\{ \frac{du_1}{d\theta} - (n+1)v_1 \right\} \right]. \quad (20)$$

The functions u_1 and v_1 must further satisfy the boundary conditions

$$u_1 = v_1 = 0, \quad \theta = \pm \alpha, \quad . \quad . \quad . \quad . \quad (21)$$

so that in general only zero values of u_1 and v_1 will satisfy equations (19), (20), and (21); the condition that there may be a non-zero solution of these equations gives a period equation which determines the possible values of n.

5. In equation (20) U can be expanded as a Fourier series, using the formula [*]

$$(kK)^2 \operatorname{sn}^2 u = K(K-E) - 2\pi^2 \sum_{m=1}^{\infty} \frac{mq^m}{1-q^{2m}} \cos \frac{m\pi u}{K},$$

in which

$$\epsilon = \frac{q + q^9 + q^{25} + \ldots}{1 + 2q^4 + 2q^{16} + \ldots}$$

and

$$1 - k^2 = \left(\frac{1-2\epsilon}{1+2\epsilon} \right)^4.$$

In the cases considered later in detail, q is small and the series above are rapidly convergent.

In the expression (12) for U it is convenient to write

$$\theta = -\alpha + \phi/\beta, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where β is chosen so that $\phi = 0, \pi$ when $\theta = \pm \alpha$. We then have

$$\beta = \frac{\pi}{2K} \left(\frac{e_1 - e_3}{6\nu} \right)^{1/2}, \quad . \quad . \quad . \quad . \quad (23)$$

while the series for U becomes

$$U = e_1 \left[1 - \frac{K-E}{k^2 K} + \frac{2\pi^2}{k^2 K^2} \sum_{m=1}^{\infty} \frac{m}{1-q^{2m}} (-q)^m \cos 2m\phi \right], \quad (24)$$

* Whittaker and Watson, 'Modern Analysis,' §§ 21.8, 22.735.

which we can write

$$U = \nu(d_0 + d_2 \cos 2\phi + d_4 \cos 4\phi + \dots). \quad (25)$$

In most of the work only the first two terms of this series are required. Expressed in terms of ϕ the equations (19) and (20) for u_1 and v_1 are

$$\left[\beta^2 \frac{d^2}{d\phi^2} + (n+1)^2 \right] \left[\beta \frac{du_1}{d\phi} - \frac{(n-1)^2}{n+1} v_1 \right]$$
$$= \frac{1}{\nu} \left[\beta^2 \frac{d^2U}{d\phi^2} v_1 - 2\beta \frac{dU}{d\phi} u_1 \right.$$
$$\left. + (n-1)U \left\{ \beta \frac{du_1}{d\phi} - (n+1)v_1 \right\} \right], \quad (26)$$

and

$$\beta \frac{dv_1}{d\phi} + (n+1)u_1 = 0, \quad \dots \quad (27)$$

while the boundary conditions are

$$u_1 = v_1 = 0, \quad \phi = 0, \pi. \quad \dots \quad (28)$$

Expanding $du_1/d\phi$ as a cosine series, we have

$$\frac{du_1}{d\phi} = a_1 \cos \phi + a_2 \cos 2\phi + a_3 \cos 3\phi + \dots, \quad (29)$$

whence

$$u_1 = a_1 \sin \phi + \frac{a_2}{2} \sin 2\phi + \frac{a_3}{3} \sin 3\phi + \dots, \quad (30)$$

and, from (27),

$$\frac{\beta v_1}{n+1} = a_0 + a_1 \cos \phi + \frac{a_2}{2^2} \cos 2\phi + \frac{a_3}{3^2} \cos 3\phi + \dots; \quad (31)$$

no constant term is necessary in the first two equations, since u_1 vanishes for $\phi = 0, \pi$. Using these expressions and (25) we can now express the right-hand side of (26) as a cosine series, and then, by solution of (26), express

$$\beta \frac{du_1}{d\phi} - \frac{(n-1)^2}{n+1} v_1$$

as a cosine series which can be compared with that derived from (29) and (31). If this is done it is easily seen that the equations fall into two independent sets, one involving only the coefficients $a_0, a_2, \dots$, the other only $a_1, a_3, \dots$ There are accordingly two distinct types of solution.

6. In the first solution

$$\frac{du_1}{d\phi} = a_2 \cos 2\phi + a_4 \cos 4\phi + a_6 \cos 6\phi + \ldots, \quad (32)$$

$$u_1 = \frac{a_2}{2} \sin 2\phi + \frac{a_4}{4} \sin 4\phi + \frac{a_6}{6} \sin 6\phi + \ldots, \quad (33)$$

and

$$\frac{\beta v_1}{n+1} = a_0 + \frac{a_2}{2^2} \cos 2\phi + \frac{a_4}{4^2} \cos 4\phi + \frac{a_6}{6^2} \cos 6\phi + \ldots \quad (34)$$

Suppose that the right-hand side of (26) is equal to

$$b_0 + b_2 \cos 2\phi + b_4 \cos 4\phi + \ldots;$$

we then have, solving (26),

$$\beta \frac{du_1}{d\phi} - \frac{(n-1)^2}{n+1} v_1$$
$$= \frac{b_0}{(n+1)^2} + \frac{b_2 \cos 2\phi}{(n+1)^2 - (2\beta)^2} + \frac{b_4 \cos 4\phi}{(n+1)^2 - (4\beta)^2} + \ldots$$
$$+ A \cos \left\{ \frac{(n+1)\phi}{\beta} \right\} + B \sin \left\{ \frac{(n+1)\phi}{\beta} \right\}, \quad (35)$$

where A and B are arbitrary constants. The complementary function must, like the other terms in the equation, be symmetrical about $\phi = \pi/2$; hence it must be of the form

$$C \cos \left\{ \frac{n+1}{\beta} \left(\phi - \frac{\pi}{2} \right) \right\},$$

and we can write

$$C \cos \left\{ \frac{n+1}{\beta} \left(\phi - \frac{\pi}{2} \right) \right\} = c_0 + c_2 \cos 2\phi + c_4 \cos 4\phi + \ldots$$

The constants C and $a_0, a_2, \ldots$ must satisfy the equation

$$a_0 + \frac{a_2}{2^2} + \frac{a_4}{4^2} + \ldots = 0, \quad \ldots \quad (36)$$

from the boundary condition for v_1, and equations

$$c_0 + \frac{b_0}{(n+1)^2} = -\frac{(n-1)^2}{\beta} a_0, \quad \ldots \quad (37)$$

$$c_{2r} + \frac{b_{2r}}{(n+1)^2 - (2r\beta)^2} = \beta a_{2r} - \frac{(n-1)^2}{\beta} \frac{a_{2r}}{(2r)^2}, \quad r = 1, 2, \ldots$$
$$\ldots \quad (38)$$

from (32), (34), and (35).

It is convenient to write

$$C' = \frac{4(n+1)}{\pi\beta^2} C \sin\left\{\frac{(n+1)\pi}{2\beta}\right\};$$

in terms of C' the coefficients c_0, c_2, c_4, ... are given by

$$c_0 = \frac{\beta^3 C'}{2(n+1)^2},$$

and

$$c_{2r} = \frac{\beta^3 C'}{(n+1)^2-(2r\beta)^2}, \quad r=1, 2, \ldots.$$

Most of the work has been done on the assumption that only the first two terms of the expression (25) for U are required, in which case we can write

$$b_0' = \qquad f_0'a_0 + g_0'a_2,$$
$$b_2' = e_2'a_0 + f_2'a_2 + g_2'a_4,$$
$$b_4' = e_4'a_2 + f_4'a_4 + g_4'a_6,$$

and similar equations; b_0', b_2', ... are written for b_0, b_2 ... to show that only terms depending on the coefficients d_0 and d_2 of (25) are included. Equations (36), (37), and (38) then take the forms

$$\frac{C'}{2(n+1)^2} + \frac{(n-1)^2}{\beta^4}a_0 + \frac{1}{(n+1)^2\beta^3}[f_0'a_0+g_0'a_2] = 0,$$

$$a_0 + \frac{a_2}{2^2} + \frac{a_4}{4^2} + \ldots = 0,$$

$$a_2\left[1 - \frac{(n-1)^2}{(2\beta)^2}\right]$$
$$+ \frac{1}{(2\beta)^2-(n+1)^2}\left[\beta^2C' + \frac{1}{\beta}\{e_2'a_0+f_2'a_2+g_2'a_4\}\right] = 0,$$

$$a_4\left[1 - \frac{(n-1)^2}{(4\beta)^2}\right]$$
$$+ \frac{1}{(4\beta)^2-(n+1)^2}\left[\beta^2C' + \frac{1}{\beta}\{e_4'a_2+f_4'a_4+g_4'a_6\}\right] = 0,$$

and so on, subsequent equations being the same in form as the last two.

There is a non-zero solution of these equations if the determinant of the coefficients of C′, a_0, a_2,... vanishes. The first four rows and columns give a condition which is usually of sufficient accuracy ; this is

$$
\begin{vmatrix}
\tfrac{1}{2}\beta^4, & \beta f_0' + (n^2-1)^2, & \beta g_0', & 0 \\[2mm]
0, & 1, & \dfrac{1}{2^2}, & \dfrac{1}{4^2} \\[3mm]
\dfrac{\beta^2}{(2\beta)^2-(n+1)^2}, & \dfrac{e_2'/\beta}{(2\beta)^2-(n+1)^2}, & 1-\dfrac{(n-1)^2}{(2\beta)^2} & \dfrac{g_2'/\beta}{(2\beta)^2-(n+1)^2} \\
 & & +\dfrac{f_2'/\beta}{(2\beta)^2-(n+1)^2}, & \\[3mm]
\dfrac{\beta^2}{(4\beta)^2-(n+1)^2}, & 0, & \dfrac{e_4'/\beta}{(4\beta)^2-(n+1)^2}, & 1-\dfrac{(n-1)^2}{(4\beta)^2} \\
 & & & +\dfrac{f_4'/\beta}{(4\beta)^2-(n+1)^2}
\end{vmatrix}
=0.
$$

$$\text{. . . (39)}$$

The coefficients f_0', g_0', ... are given in terms of d_0 and d_2 by the following equations:

$$\beta f_0' = -(n-1)(n+1)^2 d_0,$$

$$\frac{f_2'}{\beta} = (n-1)d_0\left[\ 1-\frac{(n+1)^2}{(2\beta)^2}\ \right],$$

$$\frac{f_4'}{\beta} = (n-1)d_0\left[\ 1-\frac{(n+1)^2}{(4\beta)^2}\ \right],$$

$$\frac{e_2'}{\beta} = -(n+1)d_2\left[\ 4+\frac{n^2-1}{\beta^2}\ \right],$$

$$\frac{e_4'}{\beta} = \frac{n-3}{2}d_2 - \frac{(n+1)d_2}{8}\left[\ 4+\frac{n^2-1}{\beta^2}\ \right],$$

$$\beta g_0' = -\tfrac{1}{8}(n-1)(n+1)^2 d_2,$$

$$\frac{g_2'}{\beta} = \frac{nd_2}{2} - \frac{(n+1)d_2}{32}\left[\ 4+\frac{n^2-1}{\beta^2}\ \right].$$

7. From equation (39) can be found approximately the values of n which make possible a non-zero solution of the type so far considered. Corresponding to the values

ν, 2ν, 4ν, and 8ν of e_1, the values of β^2, q, d_0, d_2, and d_4 are tabulated below :

e_1	ν	2ν	4ν	8ν
β^2	1·2479	1·4930	1·9790	2·9437
q	0·00834	0·01394	0·02102	0·02822
d_0	0·49166	0·97212	1·9160	3·7746
d_2	−0·49992	−0·99944	−1·9973	−3·9904
d_4	0·00834	0·02786	0·08392	0·22503

It will be seen that q is in all cases small, and that in consequence d_4, which is neglected in (39), is small in comparison with d_0 and d_2.

The following table and fig. 1 show the variation with n of the determinant, Δ_4, of equation (39).

Values of Δ_4.

	$e_1 = \nu$.	$e_1 = 2\nu$.	$e_1 = 4\nu$.	$e_1 = 8\nu$.
$n = -2 \cdot 0$	0·371	− 0·595	− 4·55	− 20·7
$n = -1 \cdot 5$	−16·6	−20·4	−29·6	−53·4
$n = -1 \cdot 0$	− 0·125	− 0·487	− 1·99	− 7·91
$n = -0 \cdot 5$	33·9	41·6	56·5	85·7
$n = 0$	54·6	70·2	101	165
$n = 0 \cdot 5$	41·7	57·6	90·3	159
$n = 1 \cdot 0$	0·242	0·975	3·81	15·0

It will be seen from fig. 1 that there are, corresponding to each value of e_1, three possible values of n, and that these values, approximately -2, -1, and 1, are nearly independent of the value of e_1. The proximity of the last two values to ± 1 suggested the possibility that ± 1 might be exact roots of the period equation.

In case $n = 1$ a determinant of six rows and columns was therefore used in place of Δ_4, a highly accurate approximation being made to U by including the terms depending on d_4 and d_6. It was evident from the result

that for all values of e_1 the root of the period equation was exactly unity. It then seemed clear that, corresponding to this value of n, there must be an exact solution of the equations. It was ultimately found that this was the case, and that the solution was one of a number given by Hamel * for the case of approximately radial flow not restricted by rigid boundaries. The solution given by Hamel is, in the notation of this paper,

$$u_1 = U', \quad v_1 = -2U ;$$

Fig. 1.
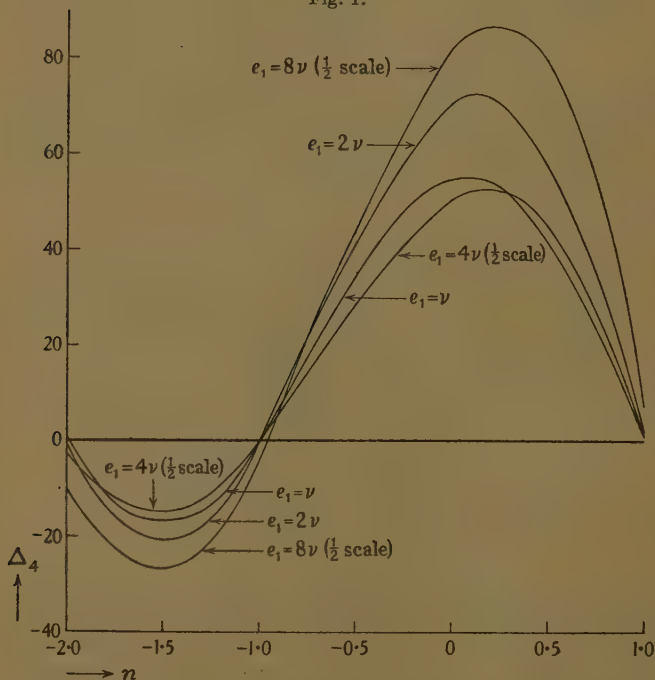
when $n = 1$, these expressions satisfy (19), and satisfy (17) since, from § 2,

$$U''' + 4U' = -\frac{2}{\nu} UU'.$$

Equation (18) merely determines the excess pressure.

* *Loc. cit.* p. 58.

It is, however, accidental that the solution of §§6, 7 coincides, when $n=1$, with Hamel's exact solution. This is a consequence merely of the special choice $e_2=0$, which was made to give a detailed illustration of the method; from (12) it follows that one result of this choice is that at the walls, $\theta=\pm\alpha$, of the channel U′ vanishes as well as U. Hamel's solution in this special case therefore satisfies the boundary conditions (21). The solution of §§ 6, 7 applies whatever the real value of e_2, and, if e_2/ν were small, but not exactly zero, would evidently lead to a value of n nearly unity; in such a case Hamel's solution would not satisfy the boundary conditions. As the numerical work was merely illustrative, it hardly appeared necessary to repeat it selecting a different value of e_2.

The other two values of n are approximately -2 and -1. It has been verified by a more accurate calculation that -2 is not an exact value of n; the actual values of n differ slightly from -2, and depend to some extent on the value of e_1. The value -1 is evidently exact, and corresponds to another solution obtained by Hamel. The solution in this case can be seen to be

$$u_1=\mathrm{U}',\quad v_1=0,$$

and gives another radial motion. The present paper is concerned, however, only with solutions in which the values of n are positive.

8. This paper is a part of some work lately undertaken to examine the stability of divergent flow. It is well known that divergent flow is in practice highly unstable, and it therefore seemed likely that the flow might in some cases be found to be unstable for small disturbances. The work above follows on the lines of some known cases in which instability for small disturbances has been inferred from the existence of neighbouring *steady* motions[*], but although it is shown above, and also subsequently in §10, that there are steady motions differing slightly from divergent radial flow, their existence is not found to depend on some critical velocity being exceeded in the radial flow. Although it will be remembered that we

[*] See, for example, G. I. Taylor, Phil. Trans. Roy. Soc. A, ccxxiii. pp. 289–343 (1923), and the author, Proc. Roy. Soc. A, cxxi. pp. 402–420 (1928).

consider above not four different motions in the same channel, but four motions all of the same type in different channels, with the result that the possibility that the four motions may all be critical cases is not excluded, there does appear to be a fundamental difference between the type of divergent flow examined here and the annular motions examined in the two papers cited. A further difference between the annular and the divergent motions is found in the type of the small disturbances ; in the annular motions these were in all cases independent of distance measured in the direction of flow, while here the disturbances are proportional to powers of the distance. It follows that the existence of some of the steady motions of §§ 6, 7, 10 does not affect the question of stability. In practice, in any divergent flow, the fluid enters the channel across a surface $r=a$, and leaves across a surface $r=b$, where $b>a>0$; let us assume this here, and so avoid the difficulties, apparent rather than real, associated with the zero value of r. If, when the velocity-distribution at entry is slightly disturbed, the disturbance decreases with increasing distance down-stream, so that at a sufficient distance from the opening of the channel the flow is radial, the radial motion is stable for the given type of initial disturbance. Some of the steady motions of §§ 6, 7, 10 correspond to negative values of n, and, therefore, give disturbances which decrease down-stream; for these disturbances the radial flow is stable. Only solutions with positive values of n can provide any evidence of instability, and such solutions are found both in §§ 6, 7 (Hamel's exact solution) and later in § 10.

The existence of the solutions with positive values of n would not be remarkable, and could scarcely be held to show instability, if the excess pressure p' were of the same order of magnitude as u', v', the alterations in velocity ; but it appears from (16) that whereas u' and v' are proportional to r^n, p' is proportional to r^{n-1}. In the solution of §§ 6, 7 $n=1$, so that the excess pressure in the disturbed motion is independent of r ; by choice of the arbitrary constant the excess pressure can clearly be made small in comparison with the maximum pressure-difference in the radial motion. This will imply that u_1 and v_1 are small, but the velocity components are ru_1 and rv_1 and will increase down-stream, nominally without limit if b/a is large ; in fact, for too large a value of r/a, ru_1, and

rv_1, since they are derived from approximate equations, will no longer be sufficiently accurate expressions for the alteration in velocity, but, nevertheless, a finite departure from radial flow is indicated by the solution. This finite departure is the consequence of a small change in the velocity-distribution at entry, and is accompanied by an excess pressure small in comparison with the maximum pressure-difference in the radial motion ; it therefore appears to show that the radial flow is unstable for this type of disturbance.

The same conclusion must be drawn from the solution of § 10 ; here the positive values of n are in all four cases greater than unity, so that p' increases down-stream as well as u' and v'. The increase in u' and v' is, however, faster than that in p'. The arbitrary constant must in this case be adjusted so that the excess pressure at $r=b$ is small in comparison with the maximum pressure-difference in the radial motion ; this requires that $p_1(b/a)^{n-1}$ shall be small. It follows that $u_1(b/a)^{n-1}$ and $v_1(b/a)^{n-1}$ must be small, but $u_1(b/a)^n$ and $v_1(b/a)^n$, the final values of u' and v', will be large if b/a is large. Again here we have an indication of a finite departure from radial flow, and, therefore, of the instability of the radial flow.

9. It is, perhaps, desirable to calculate the pressure in the radial motion, since with it must be compared the excess pressure in the disturbed motion *. From § 2

$$\frac{\partial}{\partial \theta}\left(\frac{p}{\rho}\right) = \frac{2\nu}{r^2}\, \mathrm{U}',$$

whence

$$\frac{p}{\rho} = \frac{2\nu}{r^2}\mathrm{U} + \phi(r).$$

We have also

$$\frac{\partial}{\partial r}\left(\frac{p}{\rho}\right) = \frac{1}{r^3}\left(\nu\mathrm{U}'' + \mathrm{U}^2\right),$$

so that

$$r^3\phi'(r) = \nu(\mathrm{U}'' + 4\mathrm{U}) + \mathrm{U}^2.$$

* The pressure in the general case has been calculated by W. J. Harrison, Proc. Camb. Phil. Soc. xix. pp. 307–312 (1919).

Differentiating equation (5) with regard to θ, we have

$$3\nu U'' = -3U^2 + 2(e_1 + e_2 + e_3)U - (e_2 e_3 + e_3 e_1 + e_1 e_2)$$
$$= -3U^2 - 12\nu U - (e_2 e_3 + e_3 e_1 + e_1 e_2),$$

so that

$$r^3 \phi'(r) = -\tfrac{1}{3}(e_2 e_3 + e_3 e_1 + e_1 e_2)$$

and

$$\phi(r) = A + \frac{1}{6r^2}(e_2 e_3 + e_3 e_1 + e_1 e_2),$$

where A is constant. In the special case of the previous work, $e_2 = 0$, hence

$$e_3 = -(6\nu + e_1),$$
$$U = e_1 \cos^2 \psi.$$

It follows that, ignoring the constant A,

$$\frac{p}{\rho} = \frac{e_1}{r^2}\left[\nu \cos 2\psi - \frac{e_1}{6}\right].$$

At the walls of the channel $\psi = \pm\pi/2$, so that with the values ν, 2ν, and 4ν of e_1 there is a change in the sign of the pressure across any surface where r is constant. In these cases there is nothing that corresponds to the pressure-gradient in the motion, for instance, of fluid through a channel bounded by parallel walls. The maximum pressure-difference is here the difference between the greatest and least pressures at $r = a$. If $e_1 = 8\nu$, there is no change in sign, and the maximum pressure-difference is found between two points, one at each end of the channel.

The unusual pressure-distribution is, of course, a consequence of the special type of divergent flow considered ; it has been seen that at the boundaries $U' = 0$, and a normal pressure-distribution would evidently not lead to such a condition.

10. In the second solution

$$\frac{du_1}{d\phi} = a_1 \cos\phi + a_3 \cos 3\phi + \dots,$$

$$u_1 = a_1 \sin\phi + \frac{a_3}{3}\sin 3\phi + \dots,$$

and
$$\frac{\beta v_1}{n+1} = a_1 \cos\phi + \frac{a_3}{3^2}\cos 3\phi + \dots$$

If we now write

$$b_1 \cos\phi + b_3 \cos 3\phi + \dots$$

for the right-hand side of (26), we have

$$\beta\frac{du_1}{d\phi} - \frac{(n-1)^2}{n+1}v_1 = \frac{b_1\cos\phi}{(n+1)^2-\beta^2} + \frac{b_3\cos 3\phi}{(n+1)^2-(3\beta)^2} + \dots$$
$$+ L\sin\left\{\frac{n+1}{\beta}\left(\phi-\frac{\pi}{2}\right)\right\},$$

a complementary function being taken which can be expanded in the form

$$c_1\cos\phi + c_3\cos 3\phi + \dots.$$

If

$$\pi L' = 4(n+1)L\cos\left\{\frac{(n+1)\pi}{2\beta}\right\},$$

the constants $c_1, c_3, \dots$ are given in terms of L' by

$$c_{2r+1} = \frac{\beta L'}{(n+1)^2 - (2r+1)^2\beta^2}, \quad r = 0, 1 \dots$$

The equations that must be satisfied are now

$$\beta a_{2r+1}\left[1 - \frac{(n-1)^2}{(2r+1)^2\beta^2}\right] + \frac{b_{2r+1}+\beta L'}{(2r+1)^2\beta^2-(n+1)^2} = 0,$$
$$r = 0, 1, \dots, \quad \quad (40)$$

together with the condition,

$$a_1 + \frac{a_3}{3^2} + \dots = 0, \quad \dots \quad (41)$$

that v_1 should vanish at the boundaries.

Assuming, as in most places before, that only the first two terms in the expression (25) for U are required, and denoting by $b_1', b_3', \dots$ the parts of $b_1, b_3, \dots$ that arise from these two terms, we have

$$b_1'/\beta = f_1'a_1 + g_1'a_3,$$
$$b_3'/\beta = e_3'a_1 + f_3'a_3 + g_3'a_5,$$
$$b_5'/\beta = e_5'a_3 + f_5'a_5 + g_5'a_7,$$

and so on, where

$$f_1' = (n-1)d_0 \left[1 - \frac{(n+1)^2}{\beta^2} \right] - d_2 \left[\frac{3n+1}{2} + \frac{(n-1)(n+1)^2}{2\beta^2} \right],$$

$$f_3' = (n-1)d_0 \left[1 - \frac{(n+1)^2}{(3\beta)^2} \right],$$

$$f_5' = (n-1)d_0 \left[1 - \frac{(n+1)^2}{(5\beta)^2} \right],$$

$$e_3' = \frac{n-5}{2}d_2 - 2(n+1)d_2 \left[1 + \frac{n^2-1}{4\beta^2} \right],$$

$$e_5' = \frac{3n-7}{6}d_2 - \frac{2}{9}(n+1)d_2 \left[1 + \frac{n^2-1}{4\beta^2} \right],$$

$$g_1' = \frac{3n+1}{6}d_2 - \frac{2}{9}(n+1)d_2 \left[1 + \frac{n^2-1}{4\beta^2} \right],$$

$$g_3' = \frac{5n-1}{10}d_2 - \frac{2}{25}(n+1)d_2 \left[1 + \frac{n^2-1}{4\beta^2} \right].$$

It may be assumed from §§ 6, 7 that a period equation of sufficient accuracy will be given by the first four rows and columns of the infinite determinant formed by the coefficients in equations (40) and (41), in which case the equation for n is

$$\begin{vmatrix} 1, & \beta^2-2n^2-2 & g_1', & 0 \\ & +N+f_1', & & \\ 0, & 1, & \dfrac{1}{3^2}, & \dfrac{1}{5^2} \\ 1, & e_3', & 9\beta^2-2n^2-2 & g_3' \\ & & +f_3'+N/9, & \\ 1, & 0, & e_5', & 25\beta^2-2n^2-2 \\ & & & +f_5'+N/25 \end{vmatrix} = 0,$$

where $\qquad\qquad \beta^2 N = (n^2-1)^2.$

Values of the four-row determinant, Δ_4, are tabulated below and shown in fig. 2.

It is clear from the figure that a possible value of n is nearly -2, though a comparison with the corresponding values in the first solution, in case $n=1$, makes it appear unlikely that the actual value of n is exactly -2; the actual value probably increases to some extent with e_1. Negative values of n are not, however, of interest from the present point of view.

Fig. 2 shows the smallest positive values of n satisfying the period equation; the value increases with the value

Values of Δ_4.

	$e_1=\nu$.	$e_1=2\nu$.	$e_1=4\nu$.	$e_1=8\nu$.
$n=-2\cdot0$ ..	0·398	1·62	6·61	27·0
$n=-1\cdot0$ ..	142	194	320	664
$n=0$	248	349	596	1280
$n=1\cdot0$	185	298	601	1510
$n=2\cdot0$	31·8	95·4	—	—
$n=2\cdot5$	−16·7	3·57	144	—
$n=3\cdot0$	—	—	−16·1	499
$n=4\cdot0$	—	—	—	−250

Fig. 2.
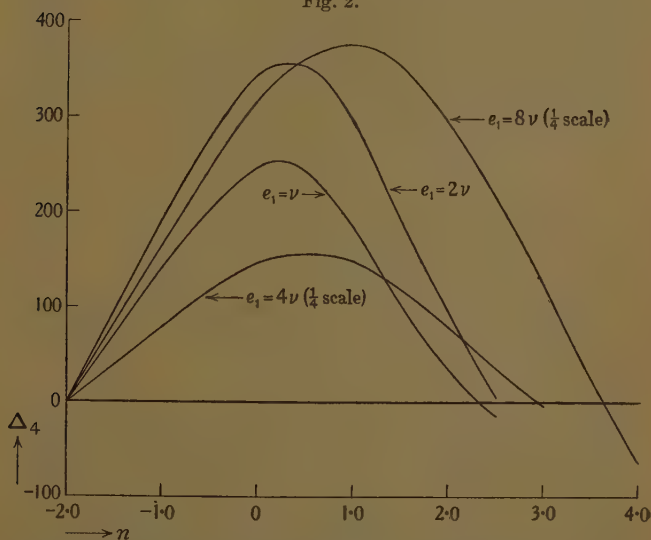
of e_1 from $2\cdot3$ when e_1 is ν up to $3\cdot6$ when e_1 is 8ν. In this solution we therefore have values of n greater than unity, so that the excess pressure increases down-stream. The solution is discussed from the point of view of the stability of the radial flow in §8.

LXXIII. *Factors determining Electrolytic Dissociation and the Energy of Dissociation of Salt Molecules. By* W. J. C. ORR, *B.Sc., Carnegie Research Scholar, and* J. A. V. BUTLER, *D.Sc., Lecturer, University of Edinburgh* *.

Introduction.

IT is known that the salts of ions which have the inert gas structure behave as strong electrolytes both in water and in a number of hydroxylic and other solvents, but an entirely different state of affairs is found among the salts of metals of the transitional series. Even in aqueous solution the halide salts of some of these metals, *e. g.*, cadmium, mercury, lead, are weak electrolytes, and the somewhat scanty conductivity data available, and the results of spectroscopic investigations [1] indicate that in methyl and ethyl alcohols they are still weaker. It appeared to us that an examination of the factors determining this broad difference of behaviour of the two classes of salts might throw much light on the conditions under which electrolytic dissociation occurs.

$$
\begin{array}{ccc}
& D_V & \\
(MX) & \longrightarrow & M^+ + X^- \quad \text{Vapour.} \\
\uparrow H_M & & \uparrow \Sigma H_I \\
MX & \xrightarrow{I} & M^+ + X^- \quad \text{Solution.}
\end{array}
$$
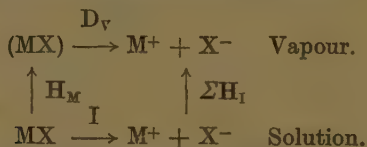
It can be seen from the above scheme that the energy of ionization of a salt in solution in a given solvent is

$$I = D_V - (\Sigma H_I - H_M),$$

where D_V is the energy of dissociation of the salt in the vapour state, ΣH_I the sum of the solvation energies of the ions, and H_M the solvation energy of the undissociated salt molecules. Little is known about the magnitude of H_M, but from general considerations it may be expected usually to be considerably less than the solvation energies of the ions. Neglecting this term, the energy available for the ionization of a molecule of the salt in the solution may be taken as approximately $\Sigma H_I - D_V$. Values of this quantity for a number of

salts in aqueous solution at 25° are given in Table I. The sources of the D_V values are stated below. The hydration energies were calculated from the lattice energies given by Sherman [2] and the heats of solution given in Int. Crit. Tables.

TABLE I.

	D_V.	ΣH_I.	$\Sigma H_I - D_V$.	$100(\Sigma H_I - D_V)/\Sigma H_I$.
LiCl	146	202	56	27·7
LiBr	137	194	57	29·4
LiI	134	186	52	28·0
NaCl	126	179	53	29·6
NaBr	121	171	50	29·3
NaI	113	162	49	30·2
KCl	112	160	48	30·0
KBr	108	153	45	29·4
KI	102	144	42	29·2
TlCl	135	161	26	16·1
TlBr	136	153	17	11·0
TlI	135	144	9	6·3
AgF	158	226	68	30·1
AgCl	147	191	44	23·0
AgBr	151	183	32	17·5
AgI	156	174	18	10·3
$ZnCl_2$	585	645	60	9·3
$CdCl_2$	540	591	51	7·8
CdI_2	517	562	45	8·0
$PbCl_2$	469	514	45	8·8
PbI_2	453	483	45	6·8

It is evident that in the case of salts of the alkali metals the sum of the hydration energies of the ions is considerably greater than the energy of dissociation of the salt molecule, the average difference being about 30 per cent. of ΣH_I. Among the other salts this ratio is considerably smaller, the average value for the salts of thallium and silver being 16 per cent., and for the salts of zinc, cadmium, and lead only 8 per cent. Even

allowing for an appreciable value of H_M there is thus ample energy available for the ionization of the alkali halides in aqueous solution, but the margin is much smaller in the other cases, and a comparatively small value of H_M would be sufficient to make them weak electrolytes. The difference between the two groups would be accentuated in a solvent in which the solvation energies of the ions are less than in water. Thus, if the solvation energies of the ions were less than in water by a constant ratio of, say, 10 per cent., as may well be the case in ethyl alcohol, $\Sigma H_I - D_V$ would still be positive for the alkali metals, but would be negative for the halides of zinc, cadmium, and lead. In such a case the former might be expected still to be strong electrolytes and the latter only slightly ionized.

In order to find the reason for these differences it is necessary to examine the factors which determine D_V and H_I. With regard to the latter, Bernal and Fowler [3] have recently shown that the heats of hydration of ions of each valence type are a linear function of the electrostatic potentials of water molecules in contact with the ions, which are calculated as a function of the ionic radius. It is found that the values of H_I for the ions Hg^{++}, Zn^{++}, Cd^{++} fall on nearly the same line as those for the alkaline earth ions Ca^{++}, Sr^{++}, Ba^{++}, and are thus related in nearly the same way to the ionic radius (which is taken as the radius in crystals). It might be inferred from this that the difference of the two types of salts does not arise from their heats of hydration and that the magnitude of D_V is the significant factor. This does not hold, however, for Tl^+, Ag^+, for which H_I is considerably greater than corresponds with the linear relation of Na^+, K^+, Cs^+. It will be necessary to examine these quantities in greater detail.

In this paper the factors determining D_V are considered. It has been necessary to restrict the calculations to molecules containing one positive and one negative ion, since they become excessively complicated in other cases.

Energy of Ionic Dissociation of Gaseous Salt Molecules.

The energies of ionic dissociation of gaseous salt molecules cannot be determined directly by experiment, but may be obtained indirectly at a given temperature

as the difference between the lattice energy of the crystalline salt (L) and its latent heat of vaporization (S). The lattice energies employed, which are given in Table IV., are those of Sherman [2] for the alkali halides and the halides of Tl, Ag, and Klemm's value for the halides of Au. The latent heats of vaporization of salts have been determined (1) by observations of the vapour pressure of the salt at two or more temperatures, (2) from *one* observation of the vapour pressure, which gives the free energy of the change solid (or liquid)$\rightarrow$ vapour, together with the entropies of the solid and vapour, which can be estimated from heat capacity data. The various determinations recorded are given in Table II. The values of Wartenburg and Schultz (column 1), obtained by method (1), differ considerably from the determinations by method (2) given under (2), (3), (4), and (6). A few direct determinations by Fiock and Rodebush by method (1), which are given under (5), are in good agreement with the others. The values employed in this paper, which refer to 298° K., are given under (7). For the salts of Cu^+, Ag^+, Au^+ it has been necessary to rely entirely on Klemm's values. The values of D_V so obtained are given in Table IV.

The first theoretical calculation of the energies of dissociation of D_V for the alkali halides appears to be that of Reis [5], who used the expression

$$\phi = -\frac{e^2}{r} + \frac{be^2}{r^a}$$

for the mutual potential ϕ of the ions at the distance r, and employed values of b and n taken from Born's calculation of the lattice energies of salt crystals. This expression is quite inadequate, as it neglects the important unbalanced polarization forces which adjacent ions exert on one another. This defect was largely remedied by Born and Heisenberg [6], who derived the expression

$$\phi = -\frac{e^2}{r}\left(1 + \frac{\alpha_1 + \alpha_2}{2r^3} + \frac{2(\alpha_1\alpha_2)}{r^6}\right) + \frac{be^2}{r^n},$$

in which the polarizabilities α_1, α_2 of the ions are introduced. The values of D_V obtained by these authors agreed very well with the data then available, but when compared with the values now available (Table III.) are uniformly

about 10 per cent. too high. This of course might be remedied by a different choice of the constants, but the expression also needs revision because it uses the older crystal lattice repulsive potential be^2/r^n.

TABLE II.

Heats of Vaporization of Salts (kgm. cal.).

.	298°.	293°.	291°.	0°.	298°.	0°.	298° K.	.	293°.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)		(2)
LiF	57	69	69	62	—	—	67	CuCl ...	23
LiCl	39	48	49	47	—	—	47	CuBr...	23
LiBr	40	46	47	43	—	—	45	CuI ...	23
LiI	40	51	—	39	—	47	46	AgF ...	65
NaF	61	71	72	65	—	—	69	AgCl...	60
NaCl	48	58	58	54	—	55	54	AgBr...	53
NaBr....	42	51	51	52	54	51	51	AgI ...	46
NaI......	39	48	48	48	—	50	48	AuCl...	28
KF	45	60	60	59	—	—	59	AuBr...	(25)
KCl......	44	53	53	52	52	53	52	AuI ...	(23)
KBr	41	51	51	50	50	51	50	TlCl ...	37
KI	39	48	49	48	47	48	47	TlBr ...	32
RbF	43	53	53	54	—	—	53	TlI ...	28
RbCl ...	41	51	50	53	—	—	51		
RbBr ...	39	48	49	49	—	—	48		
RbI......	39	48	48	46	—	—	47		
CsF	37	46	46	46	—	—	46		
CsCl	40	48	49	49	47	—	47		
CsBr	39	48	48	47	—	—	46		
CaI	39	48	48	47	—	—	46		

(1) Wartenburg and Schultz, *Z. Elektrochem.* xxvii. p. 568 (1921).
(2) Klemm, *Z. physik. Chem.* B, xii. p. 1 (1931).
(3) Fajans and Schwartz, *Z. physik. Chem.* Bodenstein Festband, p. 717 (1931).
(4) Mayer and Helmoltz, *Z. f. Physik.* lxxv. p. 26 (1932).
5) Fiock and Rodebush, J. Amer. Chem. Soc. xlviii. p. 2522 (1926).
(6) Beutler and Levi, *Z. physik. Chem.* B, xxiv. p. 263 (1934).

The application of quantum mechanics to problems involving repulsive potentials by Bruck [7], Unsold [8],

and London [9] has shown that the discriminating part of this potential is exponential in form. Born and Mayer [10] have recently applied a repulsive potential of the form $B(r) = b_+ b_- e^{-r \rho}$ to the calculation of the lattice energies of salts with considerable success. This is applied in a slightly modified form in the following calculation.

The potential energy of two ions may be expressed as

$$\phi(r) = A(r) + B(r), \quad \cdot \quad . \quad . \quad . \quad . \quad (2)$$

where $A(r)$, $B(r)$ are the attractive and repulsive potentials respectively. $A(r)$ may be written as

$$A(r) = -\frac{e^2}{r}\left(1 + \frac{\alpha_+ + \alpha_-}{2r^3} + \frac{2\alpha_+\alpha_-}{r^6}\right) - \frac{9}{4}\cdot\frac{\epsilon_+\epsilon_-}{\epsilon_+ + \epsilon_-}\cdot\frac{\alpha_+\alpha_-}{r^6}, \quad (3)$$

in which the first term is identical with that of Born and Heisenberg and the second is the resonance term which London [9] has deduced for the interacting electronic systems. The numerical coefficient 9/4, suggested by Born and Mayer [10], has been used instead of 3/2, as given by London. (3) can only be applied at temperatures appreciably removed from absolute zero, since at very low temperatures, as Margenau [11] has shown, it becomes necessary to modify the dipole terms.

The repulsive potential of two oppositely charged ions may be written [12] as

$$B(r) = c_0 b e^{(r_+ + r_- - r)/\rho}, \quad . \quad . \quad . \quad . \quad (4)$$

where c_0 is a constant the numerical values of which in halide salts, given by Pauling [13], are 1·375 for Li, 1·00 for Na^+, K^+, Rb^+, Cs^+, and 0·929 for Cu^+, Ag^+, Au^+, and Tl^+, and $b = 10^{-12}$ ergs. Born and Mayer first assumed r_+ and r_- to be equal to the Goldschmidt ionic radii, and on this basis derived values of ρ from the compressibilities and coefficients of expansion of the crystals. The values obtained for all the alkali halides did not differ greatly, and they took for all these salts the mean value $0·345 \times 10^{-8}$. Their values for the halide salts of other metals are given in Table V. Using these values, Huggins and Mayer [14] derived r_+ and r_- more exactly by finding the values required to give agreement with the observed lattice distances of the crystals.

If the values of r_+ and r_- and ρ, as so obtained, correctly represent the repulsive potential of two ions it should

be possible to calculate the potential energy at the equilibrium distance in the molecule (r_e) by first finding r_e by

$$\phi'(r_e) = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and inserting its value in

$$-\phi(r_e) = D_v. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The constants of Huggins and Mayer do not, however, give agreement with the experimental values of D_v when used in this way. This is perhaps not surprising on account of the complexity of the calculations for crystals, since effects not otherwise accounted for will appear in the repulsive constants.

It was therefore necessary to determine the repulsive constants *ab initio* from the experimental material. Since r_e is unknown it is impossible to proceed, as Born and Mayer did, by inserting its value in (7) to determine $r_0 = r_+ + r_-$, and calculating D_v by (8) from the values obtained. Assuming that Born and Mayer's values of ρ are appropriate, both r_e and r_0 can be determined by (7) and (8), using the experimental value of D_v. These values cannot of course be employed to calculate D_v, since they will necessarily reproduce the experimental data ; but if the theory is adequate the values of r_0 should be additive for the different ions.

The values of r_0 obtained, which are considerably greater for the alkali halides than those of Huggins and Mayer, were in fact nearly additive for these salts, and values of r_+ and r_- can be obtained when the value of one particular ion has been established. Taking Huggins and Mayer's value of r_- for F^- as the standard, the values given in Table III. give the best additive agreement with r_0 for the alkali halides. The differences between the r_- values of the halide ions are nearly the same as those of Huggins and Mayer, and therefore on this procedure the differences of r_0 mainly affect the values of the cations. No single value of r_+ is satisfactory for the positive ions in salts of Cu^+, Ag^+, Tl^+, Au^+. For reasons discussed below the values given are based on the fluorides (when available) or chlorides.

Using these values of the repulsion constants, it is now possible to calculate D_v by (8). This was done by plotting $\phi(r)$ as a function of r, and so determining its

minimum or equilibrium value. The values obtained are given in Table IV. column (5). The agreement is excellent for all the alkali halides except CsF (due possibly to faulty data) and LiF, for which the calculation fails, perhaps owing to the small internuclear distance in this salt. The calculated values of the other salts show a systematic deviation, which is discussed below.

The data used in these calculations are given in Table V. The polarizabilities are those given by Mayer and Helmoltz [15], together with Pauling's values for Cu^+, Ag^+, Au^+. The ionization potentials of the metals and the electron affinities of the halogens (given in ergs $\times 10^{-12}$, are from a paper by Rabinowitsch and Thilo [16]. No

TABLE III.

	r_{+}	r_{+} (H. & M.).		r_{-}	r_{-} (H. & M.).		r_{+}	r_{+} (H. & M.).
Li^+ ...	0·85	0·475	—	—	—	Cu^+ ...	0·66	1·179
Na^+ ...	1·20	0·875	F^- ...	1·11	1·110	Ag^+ ...	1·19	1·361
K^+ ...	1·40	1·185	Cl^- ...	1·50	1·475	Tl^+ ...	1·48	—
Rb^+ ...	1·51	1·320	Br^- ...	1·63	1·600	Au^+ ...	0·82	—
Cs^+ ...	1·71	1·455	I^- ...	1·86	1·785			

reliable value of ρ has been given for Au^+. The value used (0·200) was estimated by plotting the values for Cu^+, Ag^+, Tl^+ against the compressibility of the metal, and taking the value corresponding to the compressibility of gold.

An alternative method of calculation depends on the existence of a linear relation (fig. 1) between r_0 and r_e, viz.,

$$r_0 = 0·824 + 0·768 r_e , \quad \cdots \quad (9)$$

which holds, with one or two exceptions, for all the alkali halides, and, with only small discrepancies, for some of the other salts. By means of this relation r_0 can be eliminated from (4) and r_e and D_V determined by (7) and (8) entirely from quantities which are determined independently. The values so obtained are given in

TABLE IV.

### Observed and Calculated Energies of Dissociation.

	L^{25}.	S^{25}.	$D_V{}^{25}$.	D_V.	D_V.	r_{o}	$\mu \times 10^{18}$.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
LiF	240·1	67	173	>190	164	1·60	5·5
LiCl	193·3	47	146	150	147	2·02	5·2
LiBr	183·1	45	138	140	143	2·14	5·1
LiI	170·7	46	125	126	135	2·35	5·1
NaF	215·0	69	146	145	143	1·95	9·2
NaCl	180·4	54	126	124	124	2·45	8·6
NaBr	171·7	51	121	118	121	2·61	9·0
NaI.........	160·8	48	113	109	110	2·89	9·6
KF	190·4	59	131	133	131	2·21	8·6
KCl	164·4	52	112	113	114	2·70	9·9
KBr	157·8	50	108	108	108	2·89	10·6
KI	149·0	47	102	100	102	3·13	11·0
RbF	181·8	53	129	126	129	2·34	9·0
RbCl	158·9	51	108	109	109	2·85	10·6
RbBr	152·5	48	104	104	104	3·01	11·1
RbI.........	144·2	47	97	97	97	3·31	12·1
CsF	172·8	46	127	116	118	2·57	9·7
CsCl	148·9	47	102	101	102	3·10	11·7
CsBr	143·5	46	97·5	97	97	3·27	12·3
CsI	136·1	46	90	90	89	3·63	13·8
CuCl	228·1	23	205	205	204	1·74	1·82
CuBr	223·6	23	201	185	201	1·84	1·46
CuI.........	221·2	23	198	160	192	2·02	–
AgF	223·0	65	158	166	165	1·93	5·64
AgCl	207.3	60	147	137	143	2·38	6·84
AgBr	204·3	53	151	129	133	2·51	–·
AgI.........	201·9	46	156	117	128	2·76	–·
TlCl	170·9	37	134	136	—	—	—
TlBr	166·6	32	135	123	—	—	—
TlI	162·1	28	134	109	—	—	—
AuCl	236	28	208	209	209	1·95	2·38
AuBr	243	25	218	186	202	2·06	—
AuI.........	245	23	222	159	190	2 24	—

Table IV. columns (6) and (7). The calculated values of D_V agree with those observed within the probable

TABLE V.

	$\alpha \times 10^{24}$	$\epsilon_+ \times 10^{12}$		$\alpha \times 10^{24}$	$\epsilon_- \times 10^{12}$		$\alpha \times 10^{24}$	$\epsilon_+ \times 10^{12}$	ρ
Li⁺	0·079	119	F⁻	1·05	6·5	Cu⁺	0·43	32·6	0·223
Na⁺	0·21	75	Cl⁻	3·66	6·0	Ag⁺	1·72	33·4	0·260
K⁺	0·88	50	Br⁻	4·77	5·6	Au⁺	1·87	42·5 (est.)	0·200
Rb⁺	1·41	43	I⁻	7·10	5·2	Tl⁺	3·50	33·1	0·361
Cs⁺	2·5	42							

Fig. 1.
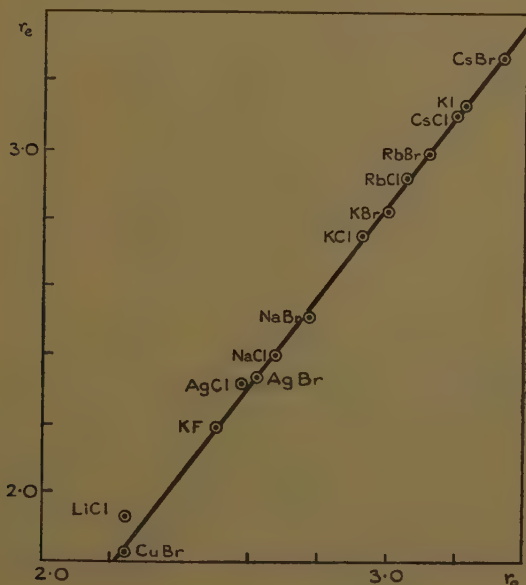
experimental error for all the halides of Na, K, Rb, and Cs, again with the single exception of CsF. Fair agreement

is obtained with AgF and the chlorides of the transitional ions, but the bromides and iodides generally show a considerable discrepancy.

Reviewing these results, we see that both methods of calculation give good agreement with the experimental values of the alkali halides, which there is every reason to believe are ionic compounds. But the calculations completely fail to account even for the sequence of values of the other salts. The experimental values of the

Fig. 2.
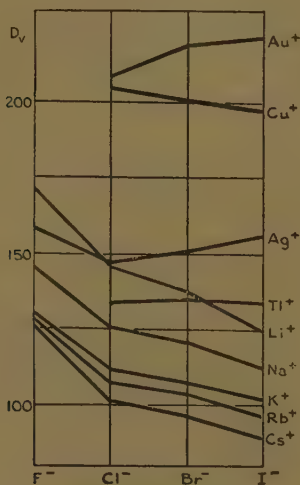
Experimental energies of dissociation of halide salts.

alkali halides (fig. 2) all decrease in the order $F > Cl > Br > I$, while the values for the transitional metal salts either increase in the order $Cl < Br < I$ or (in cuprous salts) decrease to a much smaller extent than in the case of the alkali halides. The *calculated* values also decrease in the order $F > Cl > Br > I$ in both groups irrespective of the magnitude of the characteristic constants of the metal ions. It is thus evident the salts in the second group are influenced by factors which do not come into the calculation, and they cannot therefore be regarded as having purely ionic molecules.

The agreement of the calculated values of the chlorides of these metals, given in Table IV. column 5, cannot be taken as evidence that these salts are ionic compounds, since the repulsive constants of the metals were chosen to give agreement for these salts ; but it is evident that if the calculated values of the chlorides are also too high for the ionic bond those of the bromides and iodides will deviate to an even greater extent from the experimental values than those given. Approximate agreement for some of these salts is also obtained by the second method of calculation, in which in place of empirical constants the empirical relation (9) is used. This certainly works for the alkali halides, and might be regarded as evidence of the ionic nature of the other salts with which it succeeds. But its application to these compounds may be accidental. We can conclude that the energies of dissociation of the bromides and iodides of the transitional metals under discussion are certainly greater than is required for an ionic binding, and are determined largely by other factors, such as occur in the homopolar bond. These effects occur to a considerably smaller extent, if at all, in the fluorides and chlorides. This fits in with the general conclusions as to the nature of these compounds drawn from spectroscopic [17] and crystallographic [18] evidence, and from the electrical conductivities of the pure salts [19].

We set out to find the reason for the difference of the relative magnitudes of ΣH_I and D_V (Table I.) which appear when the alkali halides are compared with those of some of the transitional metals. We have found that, while it is possible to calculate the values of D_V for the alkali halides on the assumption that the binding is ionic, the values for the other salts (except fluorides and possibly chlorides) are considerably greater than can be accounted for on this basis. It is significant that if the *calculated* values of D_V are used the ratio $R = 100 \, (\Sigma H_I - D_V / \Sigma H_I)$ approaches the value it has in the alkali halides (*cf.* Table VI.).

So far as may be judged from so few compounds this may be taken to indicate that if all these salts had the ionic binding the ratio R would approach the normal value of the alkali halides. In so far as a low value of this ratio leads to incomplete electrolytic dissociation in water and hydroxylic solvents, the latter is therefore

due to the non-ionic nature of the salt molecule. The tendency of the salts of the transitional ions to give incompletely dissociated solutions is thus due to their homopolar nature.

An interesting sidelight on the nature of these molecules is obtained by calculating their effective dipole moments from these results. When the calculated value of D_V agrees with that observed it may be considered that the value of r_e is also correct ; the effective dipole moment of the salt molecule is then given by

$$\mu = \mu_P - (\mu_+ + \mu_-),$$

where $\mu_P = e r_e$, and to the first approximation the induced

TABLE VI.

	R (expt.).	R (calc. (5)).		R (expt.).	R* (calc. (5)).
AgF	30·1	26·5	TlCl	16·1	15·5
AgCl	23·0	28·2	TlBr	11·0	19·6
AgBr	17·5	29·6	TlI	6·3	24·3
AgI	10·3	32·7			

* These figures are based on the assumption that TlCl is completely ionic. If this is not the case these figures will still be smaller than for the ionic binding.

moments in the ions are $\mu_+ = \alpha_+ e/r_e^2$, $\mu_- = \alpha_+ e/r_e^2$, so that

$$\mu = e r_e \left(1 - \frac{\alpha_+ + \alpha_-}{r_e^3} \right).$$

The values of μ so obtained from the calculated values of r_e are given in Table IV. column (10) for all the salts for which the observed and calculated values of D_V are in reasonable agreement. For the halides of Na, K, Rb, Cs the effective moment is of the order of 10×10^{-18} c.g.s. units, in agreement with the experiments of Wrede [20] on these compounds. Lithium salts and AgF, AgCl have values about half as great, the induced moments being about 25 per cent. greater than in the previous group, while in the case of cuprous salts and

AuCl the induced dipoles are almost as great as the principal dipole. The approximate calculation given above, which neglects the interaction of the induced dipoles, probably gives rather too small a value to the induced dipoles, so that in these cases the effective moment of the molecule is small.

Summary.

1. While the salts of ions having the rare gas structure are strong electrolytes in water and similar solvents, salts of metal ions of the transition series are frequently weak electrolytes even in water. This broad difference of behaviour appears to be due to the greater energy of dissociation of the salt molecule in the latter group, relative to the hydration energies of the ions.

2. An investigation is made of the factors determining the energies of ionic dissociation of simple salt molecules. The experimental values of the alkali halides, with one or two exceptions, are in agreement with the calculation, which differs from that of Born and Heisenberg by the introduction of (1) the London resonance term, (2) an exponential form of the repulsive potential similar to that used by Born and Mayer for crystals. It is possible to give a single repulsive exponent to each ion, but these differ considerably from those derived from crystal data by Huggins and Mayer. The sequence of values of the halide salts of Cu^+, Ag^+, Au^+, Tl^+ cannot, however, be accounted for on this basis. The bromides and iodides of these metals are certainly largely affected by other factors, such as homopolar binding forces, the fluorides and chlorides to a smaller extent and possibly not at all.

3. These calculations indicate that the main origin of the differences of the two groups of salts, noted in (1), is in the divergence of the salts of the second group from the simple ionic structure, *i. e.*, to their homopolar nature.

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(18) Mayer, J. Chem. Physics, i. p. 327 (1933).
(19) von Hevesy, *Z. f. Elektrochem.* xxxiv. p. 463 (1928).
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LXXIV. *The Graphic Computation of the Strength of Windows. By* A. F. Dufton, *M.A., D.I.C.**

1. **I**N connexion with the glazing of rectangular windows, a knowledge is required of the strength when subjected to uniform pressure of a rectangular plate supported at the perimeter. It is usual † to compute the strength of such a plate from the formula ‡

$$p = 2ft^2(a^2+b^2)/ka^2b^2, \quad . \quad . \quad . \quad . \quad (1)$$

where p is the uniform pressure which the pane will bear, a the length, b the breadth and t the thickness of the pane, f the modulus of rupture, and where k, the factor of safety, includes also a factor which, for glass, has the value of about 1·2.

2. In parallel coordinates, if kp/ft^2 is constant, equation (1) defines the curve enveloped by the straight line (a, b).

Transferred to cartesian coordinates, the equation expresses the condition that the straight line joining the points $(0, a)$ and $(1, b)$ shall touch the curve

$$x^{2/3} + (1-x)^{2/3} - (kp/2ft^2)^{1/3}y^{2/3} = 0. \quad . \quad . \quad (2)$$

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* Communicated by the Author.
† *Cf., e. g.,* J. R. I. Hepburn, ' Building,' viii. (10) p. 424 (1933).
‡ A. Morley, ' Strength of Materials,' London, p. 442 (1926).

3. Equation (2) defines a family of curves and, if fixed values are assigned to p and k, each particular type of glass will have its own curve. As shown in fig. 1, therefore, a simple nomogram can be constructed which will enable safe glazing sizes to be seen at a glance. In using the diagram, a straight edge (or preferably a straight line ruled on the under surface of a sheet of celluloid) is laid across so as to pass through the two points representing the length and breadth of the pane. The glass represented

Fig. 1.
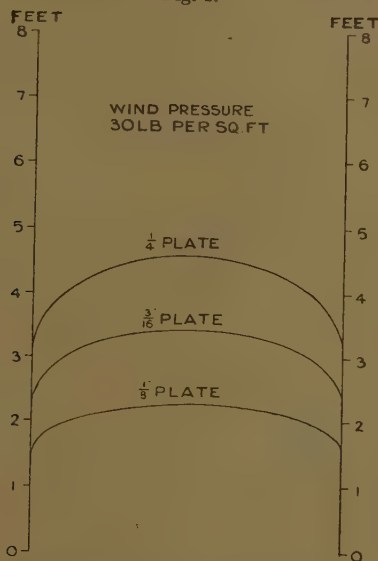
Nomogram for safe glazing sizes.

by a particular curve will then be suitable or not according as the curve projects or does not project above the straight edge.

It will be appreciated that in equation (2) the modulus of rupture is associated with the thickness of the glass and that, in consequence, the same nomogram may include glasses of the same thickness but of different strengths. In plotting the curves in fig. 1, k was taken as 4·0, p as 30 lb. per sq. ft. *, and f as 10,000 lb. per sq. in.

* *Cf.* London Building Act, 1930, 3rd Sch. (19).

4. It need scarcely be pointed out that for a particular type of glass a similar nomogram can be constructed for computing the uniform pressure which any rectangular pane will bear.

5. It is of interest that by an anamorphosis the curves of fig. 1 can be transformed into points. For equation (1) may be written

$$\begin{vmatrix} 1 & 0 & 1/a^2 \\ 0 & 1 & 1/b^2 \\ 1 & 1 & pk/2ft^2 \end{vmatrix} = 0,$$

Fig. 2.

Alignment chart for safe pressure.
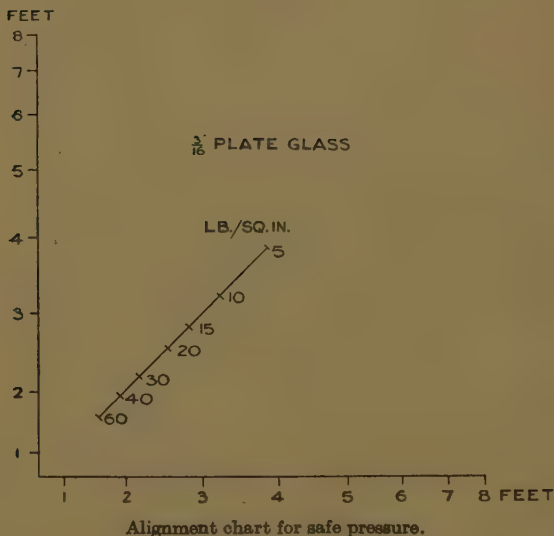
which, in parallel coordinates u and v, is the condition of collinearity of the three points

$$\begin{aligned} u & & -1/a^2 & =0, \\ & v & -1/b^2 & =0 \\ \text{and} \quad u & +v & -pk/2ft^2 & =0. \end{aligned}$$

The equation, therefore, can be solved by an alignment diagram with three parallel scales. The scales of a and b, however, are graduated in reciprocal-squares: $1/a^2$, $1/b^2$,

which, for the required range of variables, is somewhat inconvenient.

6. A different anamorphosis yields an alignment diagram which may perhaps be more convenient, particularly for computing the uniform pressure which any rectangular pane will bear. Equation (1) may be written

$$\begin{vmatrix} a^2/(a^2+c^2) & 0 & 1 \\ 0 & b^2/(b^2+c^2) & 1 \\ \dfrac{2ft^2}{4ft^2+pkc^2} & \dfrac{2ft^2}{4ft^2+pkc^2} & 1 \end{vmatrix} = 0,$$

which, in cartesian coordinates, is the condition of collinearity of the points

$$\left(\frac{a^2}{a^2+c^2},\ 0\right),\ \ \left(0,\ \frac{b^2}{b^2+c^2}\right),\ \text{and}\ \left(\frac{2ft^2}{4ft^2+pkc^2},\ \frac{2ft^2}{4ft^2+pkc^2}\right),$$

where c is an arbitrary constant.

The alignment diagram shown in fig. 2 is for the value $c=5$ ft., and shows the uniform pressure which a pane of 3/16 in. plate glass will bear.

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LXXV. *Radioactivity and Nuclear Synthesis.* By HAROLD J. WALKE, *M.Sc., Demonstrator in Physics, Washington Singer Laboratories, University College, Exeter* †.

I. *Introduction.*
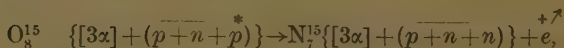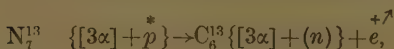
IT has been suggested in a previous paper ‡ that the elements may be considered to have been synthesized in nebulæ and stars from a primary distribution of neutons constituting a gravitating gas of zero atomic number-neuton. It has further been suggested, in view of present experimental evidence, that in none of the synthesis processes are neutrons created or destroyed, it being postulated that the total number of neutrons in the universe is fixed, this number being a fundamental cosmical constant.

By considering the gravitational instability of the neuton it has been indicated how hydrogen, diplogen and helium are first produced as a result of the formation of electron pairs by impacts between two neutrons, and in view of the experimental evidence of nuclear transformations it was shown that the isotopes of the light elements were synthesized by a multitude of reactions due to the formation of stable and unstable nuclei by absorption of protons, diplons, α-particles, and neutrons into nuclei. Synthesis, it was shown, results mainly from the formation of β-radioactive isotopes due to the addition of neutrons to certain stable isotopes.
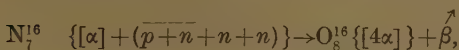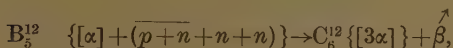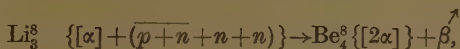
By considering the disintegration of the light elements by protons, diplons, and α-particles it has been suggested † that the stable nuclei of even atomic number consist of the maximum number of α-particles and neutrons, those of odd atomic number consisting of a diplon, the maximum of α-particles and neutrons. Among the light elements it is found that the maximum number of neutrons is two for the elements from $z=1$ to $z=16$, and four from atomic number 17 to 20. It has also been suggested ‡ that in this range of elements nuclei containing a " free " proton are radioactive by emitting positive electrons. It is now suggested, in addition, that nuclei of odd atomic number containing two neutrons as well as the diplon (in this range from $z=1-20$) are radioactive by the emission of β-radiation, the resulting nucleus consisting of the next α-particle configuration, and that nuclei of even atomic number containing three neutrons are radioactive by β-ray emission producing the next stable nucleus of odd atomic number containing a diplon and neutron. Some examples have already been considered, namely :—

$$\mathrm{L}_3^5 \quad \{[\alpha]+\overset{*}{p}\}\rightarrow\mathrm{He}_2^5\{[\alpha]+(n)\}+\overset{+\nearrow}{e,}$$

$$\mathrm{C}_6^{11} \quad \{[2\alpha]+(\overline{p+n}+\overset{*}{p})\}\rightarrow\mathrm{B}_5^{11}\{[2\alpha]+(\overline{p+n}+n)\}+\overset{+\nearrow}{e,}$$

$$\mathrm{N}_7^{13} \quad \{[3\alpha]+\overset{*}{p}\}\rightarrow\mathrm{C}_6^{13}\{[3\alpha]+(n)\}+\overset{+\nearrow}{e,}$$

$$\mathrm{O}_8^{15} \quad \{[3\alpha]+(\overline{p+n}+\overset{*}{p})\}\rightarrow\mathrm{N}_7^{15}\{[3\alpha]+(\overline{p+n}+n)\}+\overset{+\nearrow}{e,}$$

† Walke, Phil. Mag. xvii. p. 795 (1934).
‡ Walke, Phil. Mag. xviii. p. 156 (1934).

and as C_6^{11} and N_7^{13} have been obtained by diplon bombardment of B_5^{10} and C_6^{12}, it was suggested that Li_3^5 and O_8^{15} could be formed by bombarding He_2^4 and N_7^{14} with diplons, the action resulting in proton capture and neutron emission. The following radioactive isotopes were found necessary to explain the syntheses indicated :—

$$Li_3^8 \quad \{[\alpha] + \overline{(p+n} + n + n)\} \rightarrow Be_4^8\{[2\alpha]\} + \overset{\nearrow}{\beta},$$

$$B_5^{12} \quad \{[\alpha] + \overline{(p+n} + n + n)\} \rightarrow C_6^{12}\{[3\alpha]\} + \overset{\nearrow}{\beta},$$

$$N_7^{16} \quad \{[\alpha] + \overline{(p+n} + n + n)\} \rightarrow O_8^{16}\{[4\alpha]\} + \overset{\nearrow}{\beta},$$

these isotopes emitting β-radiation. It was suggested that the first two reactions could be tested by bombarding Li_3^7 and B_5^{11} with neutrons, N_7^{16} being produced by bombarding fluorine with neutrons (Harkins, Gans, and Newson).

It is now suggested that the following isotopes are radioactive, all these unstable nuclei being produced in stellar interiors by the reactions given, and it will further be indicated how these radioactive isotopes might be produced in terrestrial laboratories and where evidence has been obtained of their production. It is not suggested that all the β-radioactive isotopes are produced by the reactions given ; the various forms of neutron action are suggested as all possible. The disintegration-synthesis due to neutron capture and some particle (either proton or α-particle) emission probably occurs with high energy neutrons, though the main form of nuclear synthesis is by neutron capture, and in stellar bodies it is probable that this form of reaction is predominant, new elements being built up by the same process that allows the formation of isotopes.

## II. *Synthesis of the Elements from*
Fluorine to Potassium.

As the synthesis of the elements up to oxygen has already been considered †, we shall begin with fluorine. The absorption of a proton by oxygen O_8^{16} produces

† Walke, *loc. cit.*

" radio-fluorine," this nucleus F_9^{17} being radioactive with the emission of positive electrons as follows :—

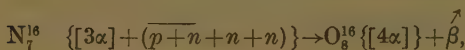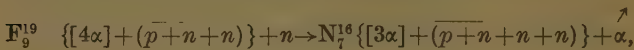$$F_9^{17} \quad \{[4\alpha]+\overset{*}{p}\} \rightarrow O_8^{17} \{[4\alpha]+n\}+\overset{+\nearrow}{e.}$$
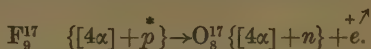
This isotope could probably be produced by the bombardment of oxygen with diplons when neutrons will be emitted. It is possible, too, since F_9^{18} is a missing isotope, that it is also radioactive and emits positive electrons. This isotope could be produced by the absorption of a proton into the nucleus of O_8^{17}. The synthesis of F_9^{19} probably occurs as a result of the β-radioactivity of O_8^{19}, this nucleus being produced by the absorption of a neutron into the O_8^{18} nucleus. The synthesis of F_9^{19} by diplon absorption could not occur, since Cockroft and Walton † have shown that the diplon entering the O_8^{16} nucleus produces O_8^{17} with the emission of a proton. Thus we have, as the synthesis process for fluorine,
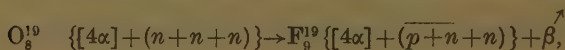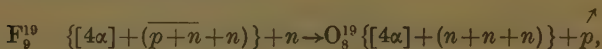
$$O_8^{19} \quad \{[4\alpha]+(n+n+n)\} \rightarrow F_9^{19} \{[4\alpha]+(\overline{p+n}+n)\}+\overset{\nearrow}{\beta}.$$
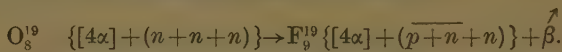
The isotope F_9^{20} produced by the absorption of a neutron into the F_9^{19} nucleus is probably β-radioactive as follows :—

$$F_9^{20} \quad \{[4\alpha]+(\overline{p+n}+n+n)\} \rightarrow Ne_{10}^{20} \{[5\alpha]\}+\overset{\nearrow}{\beta}.$$
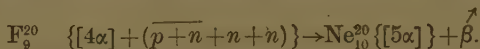
It is interesting to consider the possible radioactive isotopes which might be produced from F_9^{19} by neutron bombardment. The capture of a neutron would give the reaction suggested above. The capture of a neutron and emission of an α-particle would produce N_7^{16} (Harkins, Gans, and Newson) according to the action :—

$$F_9^{19} \quad \{[4\alpha]+(\overline{p+n}+n)\}+n \rightarrow N_7^{16} \{[3\alpha]+(\overline{p+n}+n+n)\}+\overset{\nearrow}{\alpha},$$

$$N_7^{16} \quad \{[3\alpha]+(\overline{p+n}+n+n)\} \rightarrow O_8^{16} \{[4\alpha]\}+\overset{\nearrow}{\beta},$$

whereas the emission of a proton with capture of a neutron would produce O_9^{19} thus :—

$$F_9^{19} \quad \{[4\alpha]+(\overline{p+n}+n)\}+n \rightarrow O_8^{19} \{[4\alpha]+(n+n+n)\}+\overset{\nearrow}{p},$$

$$O_8^{19} \quad \{[4\alpha]+(n+n+n)\} \rightarrow F_9^{19} \{[4\alpha]+(\overline{p+n}+n)\}+\overset{\nearrow}{\beta},$$
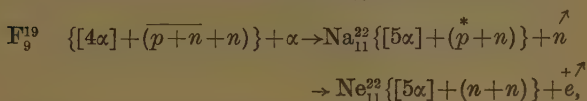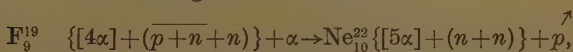
† Cockroft and Walton, Proc. Roy. Soc. A, cxliv. p. 704 (1934).

so that there are three possible β-radioactive isotopes which might result from the bombardment of fluorine by neutrons.

As the result of the absorption of a proton by F_9^{19} α-particles are emitted and O_8^{16} is produced, the reaction being :—

$$F_9^{19} \quad \{[4\alpha]+(\overline{p+n}+n)\}+p \to O_8^{16}\{[4\alpha]\}+\overset{\nearrow}{\alpha}.$$
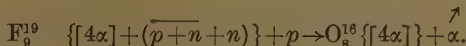
In addition, to complete the possible synthesis from fluorine we must consider the effect of α-particle absorption. The following actions occur :—

$$F_9^{19} \quad \{[4\alpha]+(\overline{p+n}+n)\}+\alpha \to Ne_{10}^{22}\{[5\alpha]+(n+n)\}+\overset{\nearrow}{p},$$

$$F_9^{19} \quad \{[4\alpha]+(\overline{p+n}+n)\}+\alpha \to Na_{11}^{22}\{[5\alpha]+(\overset{*}{p}+n)\}+\overset{\nearrow}{n}$$

$$\to Ne_{11}^{22}\{[5\alpha]+(n+n)\}+\overset{+\nearrow}{e},$$

and as a result Ne_{10}^{22} is produced, the unstable Na_{11}^{22} emitting positive electrons, the " free " proton being produced as indicated in a previous paper †.

Fluorine has been considered in detail since similar actions probably occur to cause synthesis from the elements Na_{11}^{23}, Al_{13}^{27}, P_{15}^{31}, Cl_{17}^{35}, and K_{19}^{39}. The possible actions will be given without explanation, as the arguments will be the same as those considered above, fluorine being typical of this group.

In a similar manner we can explain the synthesis of neon, N_{10}^{20} being produced by the β-radioactivity of F_9^{20}. It might, of course, be formed by the absorption of an α-particle by O_8^{16}, but at present there is no experimental evidence for such an action. Thus we have :—

$$F_9^{20} \quad \{[4\alpha]+(\overline{p+n}+n+n)\} \to Ne_{10}^{20}\{[5\alpha]\}+\overset{\nearrow}{\beta},$$
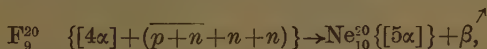
the unstable F_9^{20} being produced by the absorption of a neutron into the nucleus of F_9^{19}.

Ne_{10}^{21} is probably synthesized by the radioactivity of Na_{11}^{21}, this nucleus being produced by the absorption of a proton by Ne_{10}^{20}, *e. g.*,

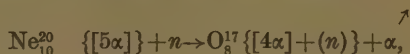$$Na_{11}^{21} \quad \{[5\alpha]+\overset{*}{p}\} \to Ne_{10}^{21}\{[5\alpha]+n\}+\overset{+\nearrow}{e}.$$
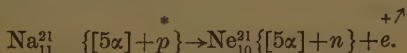
† Walke, Phil. Mag. xviii. p. 156 (1934).

Ne_{10}^{21} also arises by the absorption of a low energy neutron, or by the absorption of a diplon by Ne_{10}^{20}, thus

$$Ne_{10}^{20} \quad \{[5\alpha]\} + p + \overline{n} \rightarrow Ne_{10}^{21}\{[5\alpha]+(n)\}+\overset{\nearrow}{p},$$
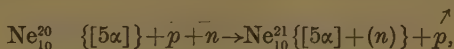
though under bombardment by high energy neutrons (corresponding to high stellar temperatures) disintegration occurs and O_8^{17} is produced as follows :—
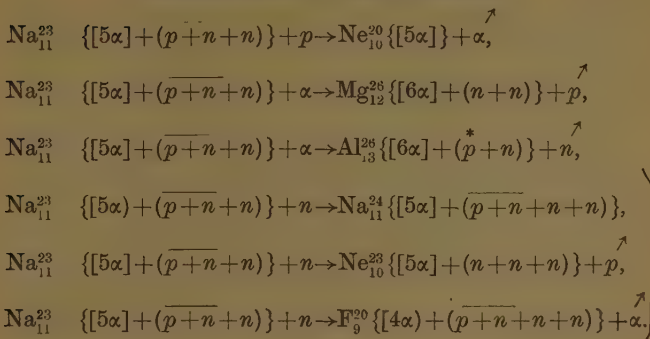
$$Ne_{10}^{20} \quad \{[5\alpha]\} + n \rightarrow O_8^{17}\{[4\alpha]+(n)\}+\overset{\nearrow}{\alpha},$$

as has been observed by Harkins, Gans, and Newson.

The heavier isotope Ne_{10}^{22} results from neutron absorption by Ne_{10}^{21} and the absorption of another neutron produces Ne_{10}^{23}, which emits β-radiation to transmute to Na_{11}^{23} :—

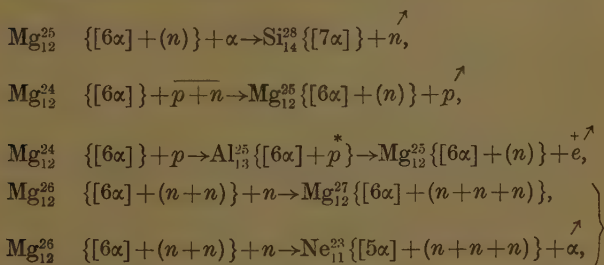$$Ne_{10}^{23} \quad \{[5\alpha]+(n+n+n)\} \rightarrow Na_{11}^{23}\{[5\alpha]+(\overline{p+n}+n)\}.$$
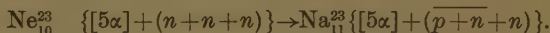
This could be tested by bombarding neon with neutrons; if capture only occurred Na_{11}^{23} would result and β-radioactivity would be observed. On the other hand, if an α-particle were first emitted O_9^{19} would be produced, so that it is possible that two β-ray products could be observed. In fact, by considering this element as typical of the elements of even atomic number and fluorine as typical of the elements of odd atomic number of the light group, we have the possibility of producing two β-ray unstable isotopes by the interaction of neutrons and nuclei of even atomic number (corresponding to simple capture and capture with α-particle emission), and of producing three β-radiaoctive isotopes by the interaction of neutrons and nuclei of odd atomic number (corresponding to simple capture, capture with proton emission and capture with α-particle emission). It is, of course, possible that under stellar conditions in which these manifold of syntheses and disintegrations are considered to occur, all these radioactive isotopes are produced and that the formation, decay, and disintegration of the unstable isotopes plays an important part in determining the relative abundance of elements.

Thus with sodium the following syntheses occur :—

$$\mathrm{Na_{11}^{23}} \quad \{[5\alpha]+(p+n+n)\}+p\rightarrow\mathrm{Ne_{10}^{20}}\{[5\alpha]\}+\alpha,$$

$$\mathrm{Na_{11}^{23}} \quad \{[5\alpha]+(\overline{p+n}+n)\}+\alpha\rightarrow\mathrm{Mg_{12}^{26}}\{[6\alpha]+(n+n)\}+p,$$

$$\mathrm{Na_{11}^{23}} \quad \{[5\alpha]+(\overline{p+n}+n)\}+\alpha\rightarrow\mathrm{Al_{13}^{26}}\{[6\alpha]+(\overset{*}{p}+n)\}+n,$$

$$\mathrm{Na_{11}^{23}} \quad \{[5\alpha)+(\overline{p+n}+n)\}+n\rightarrow\mathrm{Na_{11}^{24}}\{[5\alpha]+(\overline{p+n}+n+n)\},$$

$$\mathrm{Na_{11}^{23}} \quad \{[5\alpha]+(\overline{p+n}+n)\}+n\rightarrow\mathrm{Ne_{10}^{23}}\{[5\alpha]+(n+n+n)\}+p,$$

$$\mathrm{Na_{11}^{23}} \quad \{[5\alpha]+(\overline{p+n}+n)\}+n\rightarrow\mathrm{F_{9}^{20}}\{[4\alpha]+(\overline{p+n}+n+n)\}+\alpha.$$

The last three isotopes are β-radioactive and by β-ray emission produce the stable isotopes $\mathrm{Mg_{12}^{24}}$, $\mathrm{Na_{11}^{23}}$, and $\mathrm{Ne_{10}^{20}}$. Thus though disintegration to simpler elements takes place, progressive synthesis to magnesium occurs and the helium and hydrogen supply is kept up as indicated, $\mathrm{Mg_{12}^{25}}$ is produced from $\mathrm{Mg_{12}^{24}}$ by neutron capture, or by diplon capture with proton emission, or by the positron radioactivity of $\mathrm{Al_{13}^{25}}$ produced when $\mathrm{Mg_{12}^{24}}$ captures a proton.

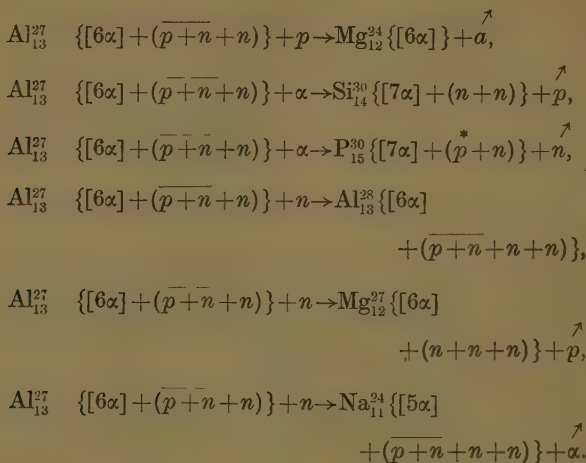From magnesium by the following actions synthesis and disintegration again proceeds :—

$$\mathrm{Mg_{12}^{25}} \quad \{[6\alpha]+(n)\}+\alpha\rightarrow\mathrm{Si_{14}^{28}}\{[7\alpha]\}+n,$$

$$\mathrm{Mg_{12}^{24}} \quad \{[6\alpha]\}+\overline{p+n}\rightarrow\mathrm{Mg_{12}^{25}}\{[6\alpha]+(n)\}+p,$$

$$\mathrm{Mg_{12}^{24}} \quad \{[6\alpha]\}+p\rightarrow\mathrm{Al_{13}^{25}}\{[6\alpha]+\overset{*}{p}\}\rightarrow\mathrm{Mg_{12}^{25}}\{[6\alpha]+(n)\}+\overset{+}{e},$$

$$\mathrm{Mg_{12}^{26}} \quad \{[6\alpha]+(n+n)\}+n\rightarrow\mathrm{Mg_{12}^{27}}\{[6\alpha]+(n+n+n)\},$$

$$\mathrm{Mg_{12}^{26}} \quad \{[6\alpha]+(n+n)\}+n\rightarrow\mathrm{Ne_{11}^{23}}\{[5\alpha]+(n+n+n)\}+\alpha,$$

$\mathrm{Mg_{12}^{27}}$ and $\mathrm{Ne_{11}^{23}}$ being β-ray emitters producing $\mathrm{Al_{13}^{27}}$ and $\mathrm{Na_{11}^{23}}$. It is significant that Fermi † has observed β-ray activity when he bombarded fluorine, sodium, and magnesium with neutrons.

Thus $\mathrm{Al_{13}^{27}}$ can readily be synthesized from magnesium,

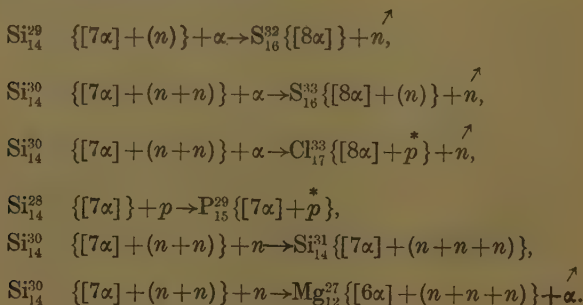† Fermi, ' Nature,' cxxxiii. p. 758 (1934).

and with this element synthesis and disintegration takes place as follows :—

$$Al_{13}^{27} \quad \{[6\alpha]+(\overline{\overline{p+n}}+n)\}+p \to Mg_{12}^{24}\{[6\alpha]\}+\overset{\nearrow}{a},$$

$$Al_{13}^{27} \quad \{[6\alpha]+(\overline{p}+\overline{n}+n)\}+\alpha \to Si_{14}^{30}\{[7\alpha]+(n+n)\}+\overset{\nearrow}{p},$$

$$Al_{13}^{27} \quad \{[6\alpha]+(\overline{p}+\overline{n}+n)\}+\alpha \to P_{15}^{30}\{[7\alpha]+(\overset{*}{p}+n)\}+\overset{\nearrow}{n},$$

$$Al_{13}^{27} \quad \{[6\alpha]+(\overline{p+n}+n)\}+n \to Al_{13}^{28}\{[6\alpha]$$
$$+(\overline{p+n}+n+n)\},$$

$$Al_{13}^{27} \quad \{[6\alpha]+(\overline{p}+\overline{n}+n)\}+n \to Mg_{12}^{27}\{[6\alpha]$$
$$+(n+n+n)\}+\overset{\nearrow}{p},$$

$$Al_{13}^{27} \quad \{[6\alpha]+(\overline{p}+\overline{n}+n)\}+n \to Na_{11}^{24}\{[5\alpha]$$
$$+(\overline{p+n}+n+n)\}+\overset{\nearrow}{\alpha}.$$

Al_{13}^{28}, Mg_{12}^{27}, and Na_{11}^{24} being radioactive by emitting β-rays as already suggested. Fermi † has detected β-ray activity of aluminium under neutron bombardment. Thus Si_{14}^{28} and Si_{14}^{30} can be synthesized and Si_{14}^{29} is probably produced from P_{15}^{29} by positron emission, when Si_{14}^{28} captures a proton, or from the same isotope by diplon capture and proton emission.

During stellar synthesis with silicon the following actions probably take place :—
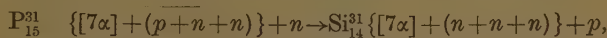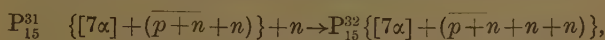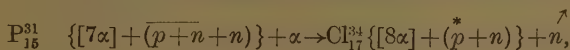
$$Si_{14}^{29} \quad \{[7\alpha]+(n)\}+\alpha \to S_{16}^{32}\{[8\alpha]\}+\overset{\nearrow}{n},$$

$$Si_{14}^{30} \quad \{[7\alpha]+(n+n)\}+\alpha \to S_{16}^{33}\{[8\alpha]+(n)\}+\overset{\nearrow}{n},$$

$$Si_{14}^{30} \quad \{[7\alpha]+(n+n)\}+\alpha \to Cl_{17}^{33}\{[8\alpha]+\overset{*}{p}\}+\overset{\nearrow}{n},$$

$$Si_{14}^{28} \quad \{[7\alpha]\}+p \to P_{15}^{29}\{[7\alpha]+\overset{*}{p}\},$$

$$Si_{14}^{30} \quad \{[7\alpha]+(n+n)\}+n \to Si_{14}^{31}\{[7\alpha]+(n+n+n)\},$$

$$Si_{14}^{30} \quad \{[7\alpha]+(n+n)\}+n \to Mg_{12}^{27}\{[6\alpha]+(n+n+n)\}+\overset{\nearrow}{\alpha}.$$
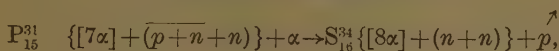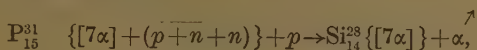
† Fermi, *loc. cit.*

The two isotopes Cl_{17}^{33} and P_{15}^{29} are positron emitters producing the stable isotopes S_{16}^{33} and Si_{14}^{29}; Si_{14}^{31} and Mg_{12}^{27} being β radioactive, the resulting isotopes being P_{15}^{31} and Al_{13}^{27}. Fermi † has detected β-ray activity from silicon bombarded by neutrons.
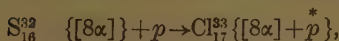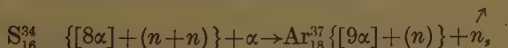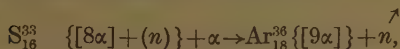
The reactions involving α-particles only occur at very high stellar temperatures, so that in the main synthesis is by proton, diplon, and neutron capture, and of these the most fundamental is that of neutron capture. Thus from silicon phosphorus is mainly synthesized, though all the reactions given probably do take place.

With phosphorus the following synthesis -disintegration processes occur :—

$$P_{15}^{31} \quad \{[7\alpha] + (\overline{p+n}+n)\} + p \to Si_{14}^{28}\{[7\alpha]\} + \overset{\nearrow}{\alpha},$$

$$P_{15}^{31} \quad \{[7\alpha] + (\overline{p+n}+n)\} + \alpha \to S_{16}^{34}\{[8\alpha] + (n+n)\} + \overset{\nearrow}{p},$$

$$P_{15}^{31} \quad \{[7\alpha] + (\overline{p+n}+n)\} + \alpha \to Cl_{17}^{34}\{[8\alpha] + (\overset{*}{p}+n)\} + \overset{\nearrow}{n},$$

$$P_{15}^{31} \quad \{[7\alpha] + (\overline{p+n}+n)\} + n \to P_{15}^{32}\{[7\alpha] + (\overline{p+n}+n+n)\},$$

$$P_{15}^{31} \quad \{[7\alpha] + (\overline{p+n}+n)\} + n \to Si_{14}^{31}\{[7\alpha] + (n+n+n)\} + p,$$

$$P_{15}^{31} \quad \{[7\alpha] + (\overline{p+n}+n)\} + n \to Mg_{12}^{27}\{[6\alpha] + (n+n+n)\} + \alpha$$
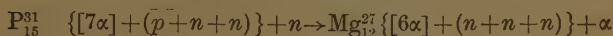
Cl_{17}^{34} emits positrons to produce S_{15}^{34}, while the three isotopes P_{15}^{32}, Al_{13}^{28}, and Si_{14}^{31} are radioactive and emit β-rays, being transformed to S_{16}^{32}, Si_{14}^{28}, and P_{15}^{31}. Thus progressive synthesis from phosphorus to sulphur takes place. S_{16}^{33} is probably formed either by the positron emission of Cl_{17}^{32} resulting from the capture of a proton by S_{16}^{32}, or by the capture of a diplon by S_{16}^{32}, the proton being emitted.

With sulphur synthesis and disintegration with the transformation of the nuclei into other stable and unstable isotopes proceeds as below :—

$$S_{16}^{33} \quad \{[8\alpha] + (n)\} + \alpha \to Ar_{18}^{36}\{[9\alpha]\} + \overset{\nearrow}{n},$$

$$S_{16}^{34} \quad \{[8\alpha] + (n+n)\} + \alpha \to Ar_{18}^{37}\{[9\alpha] + (n)\} + \overset{\nearrow}{n},$$

$$S_{16}^{32} \quad \{[8\alpha]\} + p \to Cl_{17}^{33}\{[8\alpha] + \overset{*}{p}\},$$

$$S_{16}^{34} \quad \{[8\alpha]+(n+n)\}+n \rightarrow S_{16}^{35}\{[8\alpha]+(n+n+n)\},$$

$$S_{16}^{34} \quad \{[8\alpha]+(n+n)\}+n \rightarrow Si_{14}^{31}\{[7\alpha]+(n+n+n)\}+\overset{\nearrow}{\alpha}.$$

Cl_{17}^{33} is an unstable positron emitter and is spontaneously transformed to S_{16}^{33}, while, as already discussed, Si_{14}^{31} is β-radioactive and produces P_{15}^{31}. From S_{16}^{35} synthesis to chlorine results from the β-ray emission of this isotope, Cl_{17}^{35} being produced. The chlorine isotope Cl_{17}^{36} is missing, but as Fermi has observed β-ray emission from chlorine under neutron bombardment, the period of the induced radioactivity being the longest he observed, it is probable that Cl_{17}^{36} is a radioactive product of long life. In stellar synthesis, therefore, this unstable isotope captures another neutron producing the stable Cl_{17}^{37} nucleus.

The following reactions probably occur in the synthesis and disintegration from the chlorine isotopes :—

$$Cl_{17}^{35} \quad \{[8\alpha]+\overline{(p+n}+n)\}+p \rightarrow S_{16}^{32}\{[8\alpha]\}+\overset{\nearrow}{\alpha},$$

$$Cl_{17}^{35} \quad \{[8\alpha]+(p\overset{-}{+}n+n)\}+\alpha \rightarrow Ar_{18}^{38}\{[9\alpha]+(n+n)\}+\overset{\nearrow}{p},$$

$$Cl_{17}^{35} \quad \{[8\alpha]+\overline{(p+n}+n)\}+\alpha \rightarrow K_{19}^{38}\{[9\alpha]+(\overset{*}{p}+n)\}+\overset{\nearrow}{n}.$$
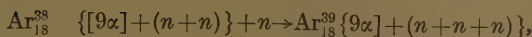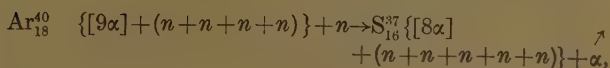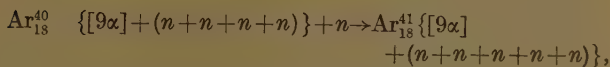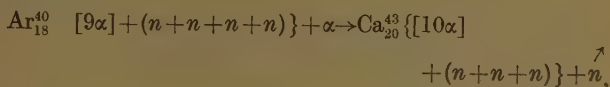
$$Cl_{17}^{35} \quad \{[8\alpha]+(\overset{---}{p+n}+n)\}+n \rightarrow Cl_{17}^{36}\{[8\alpha]+(n+n+n)\},$$

$$Cl_{17}^{35} \quad \{[8\alpha]+(\overset{-}{p+n}+n)\}+n \rightarrow S_{16}^{35}\{[8\alpha]+(n+n+n)\}+\overset{\nearrow}{p},$$

$$Cl_{17}^{35} \quad \{[8\alpha]+\overline{(p+n}+n)\}+n \rightarrow P_{15}^{32}\{[7\alpha]+(n+n+n)\}+\overset{\nearrow}{\alpha}.$$

K_{19}^{38} is radioactive and emits positive electrons producing the stable isotope Ar_{18}^{38}. Cl_{17}^{36} emits β-radiation and is transformed to Ar_{18}^{36}. Thus, as we see, Ar_{18}^{36} and Ar_{18}^{38} are synthesized from lighter elements. The last isotope has only lately been detected. The isotope Ar_{18}^{39} is, however, most probably a β-radioactive isotope of comparatively long life, allowing for the synthesis of Ar_{18}^{40} by neutron capture and being itself spontaneously transformed to K_{19}^{39}. The argon isotope of mass 38 is probably mainly synthesized cosmically by the radioactivity of Cl_{17}^{38} produced when Cl_{17}^{37} captures a neutron.
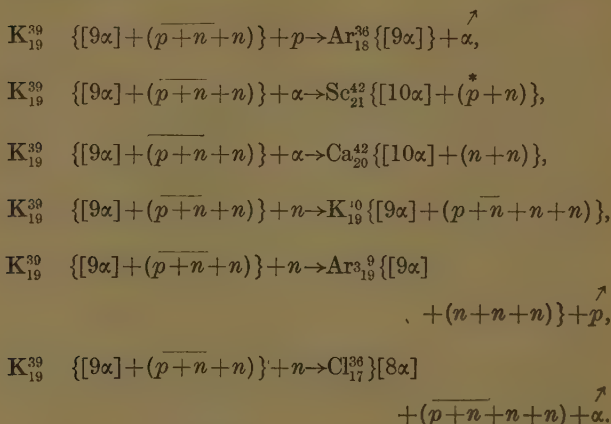
From argon the formation of other isotopes occurs as indicated :—

$$Ar_{18}^{40} \quad [9\alpha] + (n+n+n+n) \} + \alpha \rightarrow Ca_{20}^{43} \{[10\alpha]$$
$$+ (n+n+n) \} + \overset{\nearrow}{n},$$

$$Ar_{18}^{40} \quad \{[9\alpha] + (n+n+n+n) \} + n \rightarrow Ar_{18}^{41} \{[9\alpha]$$
$$+ (n+n+n+n+n) \},$$

$$Ar_{18}^{40} \quad \{[9\alpha] + (n+n+n+n) \} + n \rightarrow S_{16}^{37} \{[8\alpha]$$
$$+ (n+n+n+n+n) \} + \overset{\nearrow}{\alpha},$$

$$Ar_{18}^{38} \quad \{[9\alpha] + (n+n) \} + n \rightarrow Ar_{18}^{39} \{9\alpha] + (n+n+n) \},$$

$$Ar_{18}^{38} \quad \{[9\alpha] + (n+n) \} + n \rightarrow S_{16}^{35} \{[8\alpha] + (n+n+n) \} + \overset{\nearrow}{\alpha}.$$
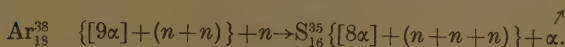
The radioactive isotopes Ar_{18}^{39} and Ar_{18}^{41} are the β-radio-active links in the general synthesis process whereby the elements are built up by neutron absorption and β-radioactivity of missing isotopes and are spontaneously transformed to K_{19}^{39} and K_{19}^{41}. Though K_{19}^{41} has been observed K_{19}^{40} is missing, and according to the hypothesis is the next β-ray synthesis isotope, being spontaneously transformed to Ca_{20}^{40}. It is perhaps significant that potassium is β-radioactive, this activity having a long half period value, the β-ray emission being usually assumed to be due to K_{19}^{41}. As, however, the isotope K_{19}^{40}, if it exists, is present in such small abundance that it has not been detected by means of the mass spectrograph, it seems probable by analogy with the induced β-ray activity of Cl_{17}^{36}, that the isotope K_{19}^{40} is the cause of the β-ray activity observed. It could be synthesized in stellar interiors by the absorption of a neutron, and as its average life is long many such nuclei would absorb another neutron, either by collision with neutrons or diplons (in which case protons would probably be emitted), to pass to K_{19}^{41} which may be stable.
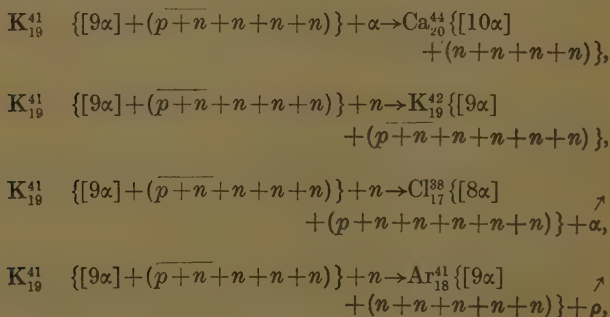
From potassium, the evolution of the elements is more difficult to describe in detail, as up to the present there is no evidence of nuclear transmutations by any particles other than neutrons. However, synthesis probably proceeds, as already indicated, as a result of the β-ray radioactivity of missing isotopes, the stable isotopes resulting from continual neutron capture. Before proceeding

to consider these elements the following actions may occur with potassium:—

$$K_{19}^{39} \quad \{[9\alpha]+(\overline{p+n}+n)\}+p \rightarrow Ar_{18}^{36}\{[9\alpha]\}+\overset{\nearrow}{\alpha},$$

$$K_{19}^{39} \quad \{[9\alpha]+(\overline{p+n}+n)\}+\alpha \rightarrow Sc_{21}^{42}\{[10\alpha]+(\overset{*}{p}+n)\},$$

$$K_{19}^{39} \quad \{[9\alpha]+\overline{(p+n}+n)\}+\alpha \rightarrow Ca_{20}^{42}\{[10\alpha]+(n+n)\},$$

$$K_{19}^{39} \quad \{[9\alpha]+(\overline{p+n}+n)\}+n \rightarrow K_{19}^{40}\{[9\alpha]+(p+\overline{n}+n+n)\},$$

$$K_{19}^{39} \quad \{[9\alpha]+(\overline{p+n}+n)\}+n \rightarrow Ar3_{19}^{0}\{[9\alpha]$$
$$\phantom{K_{19}^{39} \quad} +(n+n+n)\}+\overset{\nearrow}{p},$$

$$K_{19}^{39} \quad \{[9\alpha]+(\overline{p+n}+n)\}+n \rightarrow Cl_{17}^{36}\}[8\alpha]$$
$$\phantom{K_{19}^{39} \quad} +(\overline{p+n}+n+n)+\overset{\nearrow}{\alpha}.$$

As a result more helium is produced and, in addition, the four radioactive isotopes Sc_{21}^{42} (which emits positrons to produce Ca_{20}^{42}) and the β-ray isotopes K_{19}^{40}, Ar_{18}^{39}, and Cl_{17}^{36}, as already discussed, the first isotope being the synthesis link to form Ca_{20}^{40}.

With the heavier isotope the following actions are possible:—

$$K_{19}^{41} \quad \{[9\alpha]+(\overline{p+n}+n+n+n)\}+\alpha \rightarrow Ca_{20}^{44}\{[10\alpha]$$
$$\phantom{K_{19}^{41} \quad} +(n+n+n+n)\},$$

$$K_{19}^{41} \quad \{[9\alpha]+(\overline{p+n}+n+n+n)\}+n \rightarrow K_{19}^{42}\{[9\alpha]$$
$$\phantom{K_{19}^{41} \quad} +(p+\overline{n}+n+n+n+n)\},$$

$$K_{19}^{41} \quad \{[9\alpha]+(\overline{p+n}+n+n+n)\}+n \rightarrow Cl_{17}^{38}\{[8\alpha]$$
$$\phantom{K_{19}^{41} \quad} +(p+n+n+n+n+n)\}+\overset{\nearrow}{\alpha},$$

$$K_{19}^{41} \quad \{[9\alpha]+(\overline{p+n}+n+n+n)\}+n \rightarrow Ar_{18}^{41}\{[9\alpha]$$
$$\phantom{K_{19}^{41} \quad} +(n+n+n+n+n)\}+\overset{\nearrow}{\rho},$$

the isotopes K_{19}^{42}, Cl_{17}^{38}, and Ar_{18}^{41} being β-radioactive and of short life transmuting to the stable isotopes Ca_{20}^{42}, Ar_{18}^{38}, and K_{18}^{41}.

Thus, as can be seen, the synthesis of the elements up to calcium can be readily visualized in terms of progressive neutron addition with instability by β-ray emission of the isotopes which have been indicated. Though in many cases disintegrations also occur, as have been shown, the progressive synthesis indicates the main line of evolution, the more complex elements being built up from the simpler units, though in stellar interiors there is dynamic equilibrium between the synthesis and disintegration which proceed together. In consequence of these nuclear reactions nuclear energy is released, and it is this subatomic energy which is the source of stellar and cosmic radiation.

While it has thus been possible to discuss the manifold reactions which can, and probably do, occur in the interiors of stars and which govern synthesis and the relative abundance of the light elements, it is only possible to indicate at present the main synthesis process of the heavier elements. As, however, high energy protons, diplons, and α-particles have, as yet, not been observed to penetrate heavier nuclei than potassium, we are bound to conclude, in the light of Fermi's recent research, that the heavier nuclei are almost entirely synthesized by the continual addition of neutrons to stable nuclei, certain isotopes which are " missing " being short-lived radioactive links in a continuous synthesis process. There may, of course, be spontaneous disintegration also, so that examples of short-lived radioactive series may be found among the light elements as well as among the so-called radioactive substances.

As, further, the isotopes of the group of elements from scandium to copper have not yet been satisfactorily or completely investigated, it is proposed to omit these elements and to consider the synthesis of these nuclei when further information is available. At present it would appear probable that spontaneous disintegration by α-particle emission has been a factor in determining the isotopic constitution of this group of elements.

III. *Synthesis from Copper to the Rare Earths.*

The difficulties mentioned in considering the above-mentioned elements are not apparent in the progressive synthesis from copper upwards. The work of Fermi

already discussed probably indicates that missing isotopes are radioactive, as it can be shown that neutron capture, whether followed by the emission of nuclear components or not, produces in many cases " missing " isotopes and that all cases of radioactivity observed by Fermi are explicable on this theory. Many of the elements of odd atomic number consist of pairs of isotopes differing by two units of mass, though several consist of only one isotope. It is suggested that the missing mass number between the two isotopes is that of a β-radioactive isotope, and in many cases the addition of a neutron to the lighter isotope of such a pair produces this radioactive isotope. In most cases, too, the addition of a neutron to the heavier isotope of a pair forms another β-radioactive isotope, so that, as Fermi has observed, β-ray activity with two periods results from the interaction of neutrons with some elements.

Thus, cosmically, the synthesis from copper to zinc results from the unstable isotopes Cu_{29}^{64} and Cu_{29}^{66} produced when the stable isotopes capture a neutron. The other zinc isotopes are then produced by neutron capture, the relative abundance of the group of isotopes being determined by the stability of the separate isotopes under the continual bombardment by the ions present, and by the formation of these isotopes from both lighter and heavier elements. Zn_{30}^{69} is missing, and the last stable zinc isotope is Zn_{30}^{70}. Synthesis to gallium therefore proceeds as follows :—

$$Zn_{30}^{69} \rightarrow Ga_{31}^{69} + \overset{\nearrow}{\beta} \; ; \; Zn_{30}^{71} \rightarrow Ga_{31}^{71} + \overset{\nearrow}{\beta},$$
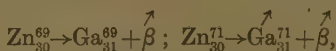
the unstable zinc isotopes being produced by the capture of a neutron by Zn_{30}^{68} and Zn_{30}^{70} respectively. It is significant that Fermi has observed β-radioactivity with both copper and zinc bombarded by neutrons.

The missing gallium isotopes Ga_{31}^{70} and Ga_{31}^{72} are β-ray links in the evolution of the elements by neutron capture and radioactive synthesis producing the stable isotopes Ge_{32}^{70} and Ge_{32}^{72}. The other germanium isotopes result from neutron absorption, the last stable isotope having mass number 76. Ge_{32}^{75} is missing, and this isotope it is postulated is radioactive to produce As_{33}^{75}. Arsenic is a single element, so that As_{33}^{76} resulting from As_{33}^{75} by neutron

capture produces Se_{34}^{76}. In addition, Ge_{32}^{77} produced by the addition of a neutron to Ge_{32}^{79} is β radioactive, and since As_{33}^{77} is also missing it is probable that the double β-ray synthesis

$$Ge_{32}^{77} \rightarrow \beta \rightarrow As_{33}^{77} \rightarrow \beta \rightarrow Se_{34}^{77}$$

takes place. It is significant that selenium has an isotope of mass 74 which does not fit in with this suggested progressive synthesis. It is perhaps possible that Ge_{32}^{73} is a β-ray emitter and that arsenic possesses a second isotope of mass 73 which exists in small abundance and has not been detected. In consequence the β-ray activity of As_{33}^{74} would produce Se_{34}^{74}. This is, however, doubtful, in spite of the fact that the Committee on Atomic Weights of the International Union of Chemistry has recently †† altered the atomic weight of arsenic to 74·91, and it is more probable that Se_{34}^{74} is produced by some secondary process and that it does not arise in the direct synthesis process.

The missing selenium isotopes Se_{34}^{79} and Se_{34}^{81} are β-ray emitters and produce Br_{35}^{79} and Br_{35}^{81}, the unstable isotopes being produced when Se_{34}^{78} and Se_{34}^{80} capture a neutron. Similarly, the missing bromine isotopes Br_{35}^{80} and Br_{35}^{82} are the synthesis links producing Xe_{36}^{80} and Xe_{36}^{82}. The other xenon isotopes are produced by the successive addition of neutrons to these nuclei. It is difficult, however, on this hypothesis to account for the isotope of mass 78 which exists in slight abundance unless the following action occurs :—

$$Br_{35}^{81} \rightarrow \beta \rightarrow \overset{*}{Kr}_{36}^{82} \rightarrow \alpha \rightarrow \overset{*}{Se}_{34}^{78} \rightarrow \beta \rightarrow Br_{35}^{78} \rightarrow \beta \rightarrow Kr_{36}^{78},$$
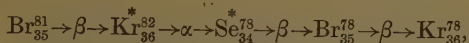
the nucleus $\overset{*}{Kr}_{36}^{82}$ formed in an excited state occasionally emitting an α-particle instead of γ-radiation, the $\overset{*}{Se}_{34}^{78}$ nucleus so formed being excited and emitting β-rays as shown.

The missing krypton isotopes Kr_{36}^{85} and Kr_{36}^{87} are β-radio-active and produce the isotopes Rb_{37}^{85} and Rb_{37}^{87}, the unstable isotopes resulting from Kr_{36}^{84} and Kr_{36}^{86} by the addition of neutrons. In the case of rubidium it seems definite that Rb_{37}^{87} is radioactive and emits β-radiation, so

†† Journ. Chem. Soc., April 1934.

Phil. Mag. S. 7. Vol. 18. No. 121. *Nov.* 1934.   3 H

that the synthesis of strontium occurs as a result of the radioactivity of Rb_{37}^{86} and Rb_{37}^{88} (missing), and Rb_{37}^{87}, the resulting nuclei being Sr_{38}^{86}, Sr_{38}^{87}, and Sr_{38}^{88}. The next synthesis link is Sr_{38}^{89}, the new nucleus formed as a result of the β-ray activity being Y_{39}^{89}, which is a simple element. Y_{39}^{90}, formed when the stable nucleus captures a neutron, is a β-radioactive isotope, the resulting nucleus being Zr_{40}^{90}. The other zirconium isotopes are formed by neutron capture, the range extending from mass number 90 to 96. The missing isotopes Zr_{40}^{93} and Zr_{40}^{95} are radioactive, producing the niobium isotopes Nb_{41}^{93} and Nb_{41}^{95} by β-ray emission. It is significant that Aston has only observed Nb_{41}^{93}, and further that Mo_{42}^{95} is an abundant isotope. It is probable, therefore, that the zirconium isotope gives rise to a double β-ray transformation thus :—

$$Zr_{40}^{95} \rightarrow \beta \rightarrow Nb_{41}^{95} \rightarrow \beta \rightarrow Mo_{42}^{95}.$$
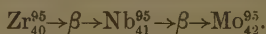
The lightest molybdenum isotope produced by direct synthesis would thus be Mo_{42}^{94} due to the β-ray activity of the missing Nb_{41}^{94}. As, however, Mo_{42}^{92} exists it is probably formed by a secondary process such as was considered to explain the existence of Kr_{36}^{78}.

The molybdenum isotopes extend from mass number 92 to 100, the isotopes of mass 99 and 101 being absent. These isotopes are β-radioactive links in the synthesis of masurium. This element is very difficult to isolate, and as yet its isotopic constitution has not been determined. It may consist, therefore, of two isotopes of mass numbers 99 and 101, the former being more abundant. Synthesis to ruthenium is thus due to the radioactivity of Ms_{43}^{100} and Ms_{43}^{102}, the corresponding isotopes being Ru_{44}^{100} and Ru_{44}^{102}. It is, of course, possible that Ms_{43}^{101} is itself missing, so that the double β-ray synthesis,

$$Mo_{42}^{101} \rightarrow \beta \rightarrow Ms_{43}^{101} \rightarrow \beta \rightarrow Ru_{44}^{101}$$
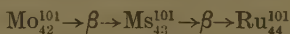
may occur. The isotopes Ru_{44}^{96} and Ru_{44}^{98} are probably produced by a secondary action arising, perhaps, as already suggested, by α-ray emission and double β-ray synthesis from Ru_{44}^{100} and Ru_{44}^{102}.

In the ruthenium group Ru_{44}^{103} is missing, the isotopes having mass numbers from 96 to 104. The isotopic constitution of rhenium has not been determined, but its atomic weight 102·9 would indicate that it is simple,

consisting of mass number 103. Thus Ru_{44}^{105}, formed when Ru_{44}^{104} captures a neutron, produces Pd_{46}^{105} by double β-ray emission, thus,

$$Ru_{44}^{105} \rightarrow \beta \rightarrow Re_{45}^{105} \rightarrow \beta \rightarrow Pd_{46}^{105}.$$
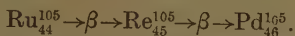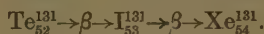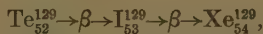
Rh_{45}^{105} is the β-ray link in the evolutionary process by means of which the lightest palladium isotope is synthesized. The isotopes of this element have not been investigated, but by analogy we would suggest that they are 104, 105, 106, 108, and perhaps 110. The missing isotopes 107 and 109, formed when the isotopes 106 and 109 capture a neutron, emit β-rays and are transformed to Ag_{47}^{107} and Ag_{47}^{109}. The missing isotopes Ag_{47}^{108} and Ag_{47}^{110} are also radioactive and produce Cd_{48}^{108} and Cd_{48}^{110}, the other cadmium isotopes being produced by neutron capture. Aston has not discovered the isotope of mass 108 which is stable on this hypothesis. However, cadmium is a very difficult element to deal with in the mass spectrograph, so that this isotope may exist but remains to be detected.

This missing isotope of cadmium Cd_{48}^{115} produces In_{49}^{115} by β-ray emission. This element is apparently simple, so that the missing isotopes In_{49}^{116} is the next β-radioactive link, by means of which tin is formed. The other isotopes are formed by neutron capture until Sn^{124} is reached. The small abundance isotopes of mass number 112, 114, and 115 are probably formed by a secondary process similar to the process suggested with krypton.

Antimony is synthesized by the β-ray emission of Sn_{50}^{121} and Sn_{50}^{123}. The isotope of mass 123 is missing, but that of mass number 121 is present in small abundance. It is therefore to be anticipated that the spontaneous β-ray activity of tin will be observed. Sb_{51}^{122} and Sb_{51}^{124}, produced by the absorption of a neutron by the stable isotopes of mass 121 and 123, are β-radioactive, and are the synthesis links which form Te_{52}^{122} and Te_{52}^{124}. The remaining tellurium isotopes result from the addition of neutrons, the range extending from mass number 122 to 130, 127 and 129 being missing.

Iodine I_{53}^{127}, I_{53}^{129}, and I_{53}^{131} are thus produced as a result of the β-ray emission from the missing tellurium isotopes, Te_{52}^{131} being produced when Te_{52}^{130} captures a neutron.

Iodine is, however, a single element of mass 127, so that it is probable that both Te_{52}^{129} and Te_{52}^{129} give rise to xenon isotopes, thus,

$$Te_{52}^{129} \to \beta \to I_{53}^{129} \to \beta \to Xe_{54}^{129},$$

$$Te_{52}^{131} \to \beta \to I_{53}^{131} \to \beta \to Xe_{54}^{131}.$$

The next radioactive isotope I_{53}^{128} is produced when I_{53}^{127} absorbs a neutron. This isotope produces Xe_{53}^{128} by emitting β-radiation, and this, on our theory, should be lightest xenon isotope. As, however, Xe_{54}^{124} is the lightest isotope observed it is probably produced by the action

$$I_{53}^{128} \to \beta \to \overset{*}{X}e_{54}^{128} \to \alpha \to \overset{*}{T}e_{52}^{124} \to \beta \to I_{53}^{124} \to \beta \to Xe_{54}^{124},$$
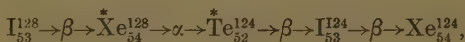
the short-lived series arising from the nucleus $\overset{*}{X}e_{54}^{124}$ formed in a state of excess energy by the production of a new nuclear α-particle †. It is suggested that some nuclei formed in this state emit the newly formed α-particle, instead of binding the particle in the nuclear core and emitting the excess energy in the form of γ-radiation. Xe_{54}^{126} is probably similarly formed from Xe_{54}^{130}, the missing iodine isotope I_{55}^{129} having sufficiently long life to allow the formation of I_{53}^{130} by neutron capture, $\overset{*}{X}e_{54}^{130}$ being then produced in a state of excess energy by the β-radioactivity of this missing iodine isotope.

The xenon isotopes extend from mass number 124 to 136 with 133 and 135 missing, these isotopes being the β-ray links to produce Cs_{55}^{133} and Cs_{55}^{135}. Cæsium, however, has only one stable isotope Cs_{55}^{133}, and in consequence we must suppose that Cs_{55}^{155} is β-radioactive and of short life, so that Xe_{54}^{135} disintegrates as follows :—

$$Xe_{54}^{135} \to \beta \to Cs_{55}^{135} \to Ba_{56}^{135};$$

it is significant that cæsium would be expected to be radioactive by analogy with potassium and rubidium. It appears, therefore, that the isotope of mass 135 was radioactive, but of short life, and has disappeared.

The other barium isotopes are produced by neutron capture, the range extending from mass number 135

† Walke, Phil. Mag. xvii. p. 1176 (1934).

to 138. The isotope of mass 139, which is missing, is a short-lived β-ray emitter and produces La_{57}^{139}. By neutron absorption the missing La_{57}^{140} is produced, and this isotope is also β-radioactive, the new isotope produced being Ce_{58}^{140}, cerium is thus evolved. the other isotope, Ce_{58}^{142}, being formed when the missing Ce_{58}^{141} captures a neutron. Ce_{58}^{141} is, however, radioactive, and by β-ray emission produces the nucleus Pr_{59}^{141}, which is almost certainly single. Synthesis then proceeds by the radioactivity of the missing Pr_{59}^{142} formed as a result of Pr_{59}^{141} capturing a neutron, the unstable isotope emitting β-radiation to form Nd_{60}^{142}. The other neodymium isotopes are produced by neutron addition.

Thus, as can be seen, the continuous synthesis of the elements proceeds naturally if we assume the β-radioactivity of missing isotopes, and except for the group from scandium to copper (whose isotopic configurations we suggest are not completely known), the synthesis of every known isotope can take place by neutron absorption. The gradual evolution of the elements is thus a result of a natural process, which process it is suggested has been in part reproduced by Fermi. These synthesis processes do not require excessively high stellar temperatures, as neutron disintegration has been observed at low energies, corresponding to the normally accepted stellar temperatures.

It is certain, therefore, that the evolution of the rare earths proceeds similarly. It is proposed, however, to consider these elements in a later paper when further information of their isotopic constitution is available.

IV. *Synthesis of the Elements from Hafnium to Lead.*

It is probable that tantalum Ta_{73}^{181} is synthesized by the β-ray activity of a missing hafnium isotope Hf_{72}^{181}. This element being single, Ta_{73}^{182}, formed when the stable isotope captures a neutron, emits β-radiation and is transformed into W_{74}^{182}. By neutron capture the other tungsten isotopes are produced, the missing mass numbers in this range being 185 and 187. These isotopes are β-radioactive links in the synthesis process and produce Re_{75}^{185} and Re_{75}^{187}. The missing isotopes of rhenium, Re_{75}^{186} and Re_{75}^{188}, are also β-radioactive and form Os_{76}^{186} and

Os_{76}^{188}. The remaining isotopes in the mass range 186–192 are produced by neutron capture. The missing osmium isotopes are Os_{76}^{191} and Os_{76}^{193}, and these probably produce the corresponding iridium isotopes as a result of the β-ray activity. Ir_{77}^{192} and Ir_{77}^{194} are the next synthesis unstable isotopes producing Pt_{78}^{192} and Pt_{78}^{194} by emitting β-radiation. The probable isotopes of platinum are therefore 192, 193 (?) 194, 195, 196, and 198, 197 and 199 being radioactive and produce Au_{79}^{197} and Au_{79}^{199}.

By neutron capture Au_{79}^{198} and Au_{79}^{200} are produced, these unstable isotopes being the radioactive links in the synthesis of mercury. Thus we should expect mercury to consist of the isotopes 198, 199, 200, 201, 202, and 204, 203 and 205 being the next β-radioactive isotopes to produce Tl_{81}^{203}, Tl_{81}^{205}. It is significant that Hg_{80}^{196} and Hg_{80}^{197} exist in small abundance and that Hg_{80}^{203} has also been detected. Hg_{80}^{197} can, of course, be formed when Hg_{80}^{196} captures a neutron, but the presence of mass number 196 suggests that this isotope is produced by some secondary process rather than by the main synthesis. It is, perhaps, possible that mercury is formed by the radioactive disintegration of heavier elements, as α-ray emission from some isotopes of atomic number 82 could produce certain isotopes of mercury. It is more probable, however, that Hg_{80}^{196} is formed during the synthesis of Hg_{80}^{200} from Au_{79}^{200}, as the emission of β-rays from the latter results in the formation of a new α-particle and this might sometimes be emitted, Hg_{80}^{196} being formed by double β-ray synthesis from the excited Pt_{80}^{196} nucleus produced. The existence of 203 also suggests that slight β-ray activity should be observed with mercury.

If thallium is stable Tl_{81}^{204} should be β-radioactive to produce the lightest lead isotope Pb_{82}^{204}, Tl_{81}^{206} formed by the stable isotope Tl_{81}^{205} capturing a neutron producing Pb_{82}^{206}. Actually Pb_{82}^{203} is also present in small abundance. This isotope may, of course, be produced as the result of a disintegration process, but it seems more probable that Hg_{80}^{203} and Tl_{81}^{203} are slightly β-radioactive, the following action occurring :—

$$Hg_{80}^{203} \rightarrow \beta \rightarrow Tl_{81}^{203} \rightarrow \beta \rightarrow Pb_{82}^{203}.$$
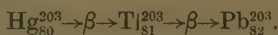
The other stable lead isotopes are produced initially by neutron capture, though enrichment of certain isotopes

by radioactive disintegration of heavier elements occurs in radiogenic leads.

The synthesis isotopes of ordinary lead would be Pb_{82}^{209} and Pb_{82}^{211} producing Bi_{83}^{209} and Bi_{83}^{211}. It is significant that Bi_{83}^{211} does not exist and that Pb_{82}^{209} is present in slight abundance. Pb_{82}^{211} therefore gives rise to Po_{84}^{211} by the action,

$$Pb_{82}^{211} \rightarrow \beta \rightarrow Bi_{83}^{211} \rightarrow \beta \rightarrow Po_{84}^{211},$$

and, further, we should expect to observe slight β-ray activity with lead due to the isotope of mass number 209.

Bi_{83}^{210} produced by Bi_{83}^{209} capturing a neutron is the β-ray synthesis link to produce Po_{84}^{210}, which on this scheme would be the lightest polonium isotope if the element of atomic number 84 were stable.

Thus, as can be seen, we can understand the synthesis of the stable elements by assuming that nuclei are mainly built up by the addition of neutrons with β-ray instability of missing isotopes, these isotopes being synthesis links in a general evolution of the nuclei from a primary cosmic distribution of neutrons, of which the total number has remained fixed, this number being a cosmical constant which is a fundamental constant of the universe.

It is probable, too, that initially the radioactive elements are synthesized similarly, as these substances differ from stable elements only because they disintegrate spontaneously.

The process we have considered, however, only indicates the main line of nuclear evolution. Many of these unstable isotopes (as well as the stable ones) are produced by disintegration, as in many cases neutron capture results in the emission of a proton or an α-particle. Thus the relative abundance of isotopes is determined by their stability under stellar conditions, and the emission of protons and α-particles preserves the supply of hydrogen and helium, allowing further synthesis to take place. For example, iron is produced by the reactions,

$$Mn_{25}^{55} + n \rightarrow Mn_{25}^{56} \; ; \; Mn_{25}^{56} \rightarrow Fe_{26}^{56} + \overset{\nearrow}{\beta},$$
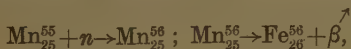
the unstable manganese isotope being formed when Mn_{25}^{55} captures a neutron, and

$$Co_{27}^{29} + n \rightarrow Mn_{55}^{26} + \overset{\nearrow}{\alpha} \; ; \; Mn_{25}^{56} \rightarrow Fe_{26}^{56} + \overset{\nearrow}{\beta},$$
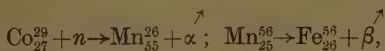
the unstable isotope arising from the disintegration of cobalt.

Thus in the formation of the elements in stars, the variations observed in isotopic abundance depend on the fact that synthesis and disintegration (with the production of stable and unstable isotopes) proceed continuously, so that the nuclear equilibrium is dynamic and not static, new nuclei being always formed and the stable nuclei when produced being continually broken down to simpler nuclei, or being changed into more complex configurations by the addition of neutrons.

V. *Stellar and Cosmic Radiation.*

As has been shown in this and a previous paper †
it is possible to indicate how the elements have probably been synthesized from the primæval gas " neuton," by a process which is common to all elements, namely, by the radioactive synthesis due to β-ray emission from missing isotopes. The formation of heavier elements is thus a natural phenomenon corresponding to the condensation of the light elements into stabler, and in general more complex, configurations as a result of the gradual increase in temperature due to various nuclear reactions. In the final state we have equilibrium and the heat energy radiated is equal to the energy emitted in the synthesis processes occurring. As has been emphasized synthesis and disintegration are occurring simultaneously, the supply of helium and hydrogen being maintained mainly by the disintegration of the light elements. The final condition of a star with respect to the abundance of elements is a result of the manifold of reactions considered, and though the abundance of particular elements remains constant relative to the others, this abundance is governed by three factors, namely :—

(i.) The synthesis of the elements from lighter nuclei ;

(ii.) their production as a result of the disintegration of heavier nuclei ;

(iii.) the disintegrations they suffer as a result of interactions with neutrons, protons, etc.

† Walke, *loc. cit.*

A feature of the whole cycle is the continual release of "mass defect" energy, which maintains stellar radiation as a result of the continuous transformation of nuclei into stabler and in general more complex configurations. The "mass defect" energy, however, does not indicate that matter, *i. e.*, ultimately neutrons, is being annihilated; it indicates merely that in all the nuclear reactions concerned the final nucleus is more stable than the nucleus produced by the absorption of a particular particle and that energy is emitted because the components of the final nucleus are more tightly bound than in the unstable nucleus produced. The nuclear energy released appears as kinetic energy of emitted particles or as γ-radiation. But, as has been already stated, the number of neutrons remains constant, as in none of the reactions which have been observed experimentally are neutrons annihilated in the form of radiation, nor are they spontaneously created by condensation from radiation.

For example, the reaction
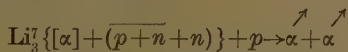
$$\mathrm{Li}_3^7 \{[\alpha] + \overline{(p+n} + n)\} + p \rightarrow \overset{\nearrow}{\alpha} + \overset{\nearrow}{\alpha}$$

indicates that

$$\mathrm{Li}_3^7 = \alpha + \overline{p+n} + n$$

$$= (4n + 2\overset{+}{e}) + (2n + \overset{+}{e}) + n$$

$$= 7n + 3\overset{+}{e},$$

and that

$$p = n + \overset{+}{e},$$

so that the left-hand side of the equation gives $8n + 4\overset{+}{e}$.

Similarly,

$$\alpha + \alpha = (4n + 2\overset{+}{e}) + (4n + 2\overset{+}{e})$$

$$= 8n + 4\overset{+}{e},$$

and the number of neutrons on the right-hand side is equal to the number on the left. Equations of this type, in which the total number of neutrons remains constant, will be satisfied by all the reactions occurring. The total number of neutrons in the universe is a fundamental cosmical constant, the number of neutrons in all the nuclei now present in the complex configurations produced by the gravitational instability of the initial

distribution of neuton being the same as it was in the beginning, and will be the same when the final state of the universe is reached.

The radiation of stars is thus maintained by nuclear re-actions similar to those observed in terrestrial laboratories by the atomic physicist ; and by the radioactivity of unstable elements.   The energy released is first emitted in the form of γ-radiation, or as kinetic energy of high speed particles.   As many of the emitted particles will have very high energy, corresponding to tremendously high stellar temperatures, it can easily be realised why reactions involving high energy bombarding particles can occur in stars at accepted stellar temperatures †. For example, the reactions considered involving α-particle energies of 5×10^6 e.v. can occur, as α-particles of much higher energy are emitted in the disintegration of the light elements by protons and diplons.   By impacts with atoms the kinetic energy of many of the nuclear projectiles is directly transformed into heat energy, by increasing the total energy of atoms, or into light and X-radiation by the ionization of atoms.   But ultimately the kinetic energy is transformed into heat and light, since any X-radiation will be degraded into radiation of longer wave-length by atomic impacts.

In many reactions γ-radiation is emitted, and this is often of high frequency.   Finally this radiation, too, will be degraded into heat and light energy, since by impacts with atoms and nuclei its frequency will always be decreased.   Thus, as a result of impacts with atomic electrons the wave-length of γ-radiation will be increased by Compton scattering, or it may be transformed into kinetic energy of an electron by photoelectric absorption. Ultimately, therefore, as a result of atomic encounters, the high frequency γ-rays are transformed into low frequency γ-radiation, X-rays, or kinetic energy of electrons. This radiation is further degraded by atomic impacts into light quanta and heat.

When such high frequency γ-rays interact with nuclei, electron pairs are formed, so that this form of radiation may disappear completely in the form of kinetic energy of electrons.   The positrons produced by such actions soon suffer annihilation by interaction with negative

† See note added in proof (p. 822).

electrons to produce quanta of energy 0.5×10^6 e.v.
or 1.0×10^6 e.v., and the negative electrons transfer
energy to atoms by ionization phenomena. Finally,
therefore, γ-radiation, even as a result of nuclear impacts,
is transformed into kinetic energy of electrons and low
frequency quanta. The latter, as already indicated,
are soon degraded into heat and light, as is the electronic
kinetic energy, since the electrons produced ionize
atoms with which they interact. Nuclear energy is
thus continuously transformed into light and heat,
and the energy of stellar radiation is to be found in the
energy of the nucleus itself.

But if the nuclear reactions take place near the surface
of stars, or in nebulæ as is possible, much of the γ-radiation
produced will be emitted and may form part of the
primary cosmic ray-beam. As, however, the mass
defect energy released in all nuclear reactions of the
type considered is of the order 10×10^6 e.v. and less,
it seems improbable that γ-radiation of energy greater
than 23×10^6 e.v. (corresponding to the production
of α-particles by the union of diplons) will be emitted.
However, a veritable spectrum of γ-radiation of lower
frequency will be produced, with strong components
corresponding to the formation of hydrogen and diplogen.
It appears, therefore, from the reasoning of this and the
previous paper already mentioned, that a γ-ray component
of cosmic radiation, should be detected, but that its energy
should not be greater than 23×10^6 e.v. It is significant
that Millikan has concluded that the cosmic ray-band
of lowest energy needed to reproduce his ionization-
depth curve, corresponds to the synthesis of helium from
hydrogen.

It has recently been shown by Compton and Stephenson†
that most of the effects observed by assuming that
cosmic radiation is photonic in nature would be observed
if the primary beam consisted of high speed ions, and
they have recently concluded that high altitude measure-
ments on cosmic radiation indicate that the primary
beam probably consists of protons of energy 2×10^9 e.v.
This is in accordance with the directional experiments
performed by Compton and Alvarez ‡ and Johnson §,

† Compton and Stephenson, Phys. Rev. xlv. p. 441 (1934).
‡ Compton and Alvarez, Phys. Rev. xliii. p. 835 (1932).
§ Johnson, Phys. Rev. xliii. p. 834 (1932).

who showed that the incoming cosmic ray-beam was predominantly positively charged.

As protons of this energy appear to form the main component of the primary beam (Johnson † concludes that 90 per cent. of the rays at the top of the atmosphere are positively charged), it is of interest to speculate how these ions may attain this energy. It seems probable that they must receive some acceleration analogous to the acceleration of protons in discharge-tubes, and they may receive such an acceleration in rapidly varying electromagnetic fields such as may exist in stellar spots, analogous to sunspots, as Swann ‡ has shown that electrons (and therefore presumably protons) could be accelerated to energies of the order 10^9 e.v. in such spots. We must therefore suppose that such high energy ions in the primary cosmic ray-beam do not represent the equilibrium temperature of stars, since they are artificially accelerated to these high energies by electro-magnetic forces in stellar spots. We might therefore reasonably expect to observe some daily variation in cosmic ray-intensity, with a maximum near noon and a minimum near midnight, since we should expect sunspots to contribute to the proton stream. There might also be some slight relation between cosmic ray-intensity and the sunspot period.

Such high energy particles would be capable of producing nuclear disintegrations, and the bursts of ionization known as Hoffmannstösse may result from collisions between these ions and nuclei.

In addition to the Hoffmannstösse, however, another phenomenon has been observed, namely, the production of showers of electrons when cosmic rays interact with nuclei. Electron pairs have been observed when γ-rays interact with the nucleus and, as it is probable that a quantum component of the primary beam exists, some of the pairs probably result from the interaction between the 23×10^6 e.v. radiation and nuclei. Furry and Carlson have shown, however, that high speed electrons are nearly as efficient in producing electron pairs as γ-radiation, and this phenomenon has been observed by Skobeltzyn and Stepanowa §. As, moreover, electrons

† Johnson, Phys. Rev. xlv. p. 758 (1934).
‡ Swann, Phys. Rev. xliii. p. 217 (1933).
§ Skobeltzyn and Stepanowa, ' Nature,' cxxxiii. p. 565 (1934).

are being continually emitted by radioactive nuclei, it is possible that an electron component of the primary cosmic ray-beam also exists, since electrons could be accelerated to high energies in stellar spots. Thus, since pairs may be formed by high energy electrons, the shower formation may result from an electron component of the primary beam, as it is probable that the γ-ray component is not of sufficiently high energy to produce the showers.

We may imagine, for example, that an electron of energy 2×10^9 e.v. splits up into two electrons of energy 1×10^9 e.v. on interaction with the potential field of a nucleus. These high energy electrons are produced in a nuclear field and may therefore both split up into two electrons of energy 5×10^8, so that a shower of four electrons would be observed. However, these electrons may also produce electron pairs since they, too, are produced in a nuclear potential field. The showers may therefore represent on a large scale the formation of a single pair of electrons.

The positive electrons produced by the showers are soon annihilated in the form of quanta of energy 5×10^5 e.v. and $1 \cdot 0 \times 10^6$ e.v., so that the atmosphere is continually ionized by secondary γ-radiations of these frequencies. At the same time ionization is produced by the negative electrons of the showers, as well as by the Hoffmannstösse already mentioned. The ionization measured is therefore largely due to secondary effects, and it seems certain that we shall only understand the true nature of the primary cosmic ray-beam if we eliminate secondary effects and concentrate attention on those rays which reach the atmosphere from interstellar space.

While, therefore, the origin of the primary beam is in the cosmos, the true nature of the beam is not certain. From the synthesis process we have considered it would appear that three components exist, a quantum beam of many frequencies limited by an energy 23×10^6 e.v., a proton beam produced by the acceleration of hydrogen ions in stellar spots, and an electron component similarly accelerated. From the reactions considered ultra γ-radiation could not form a component of the primary beam, so that the creation of matter by the condensation of quanta of high energy into a positive and negative proton could not take place. On the view-point adopted,

neutrons could not be created, as the condensation of high frequency γ-radiation would produce electron pairs, as has been verified experimentally. Speculation on the creation and annihilation of matter (*i. e.*, ultimately neutrons) is therefore merely speculation. In the light of the experimental evidence which has been considered, it would appear that the number of neutrons in the universe is constant and that synthesis proceeds by an evolutionary process, whereby neuton assumes more and more complex configurations by uniting with positive electrons to form the various nuclei as we know them.

The whole process as considered involves the liberation of nuclear energy in the form of heat and it would appear that the final state will be one of maximum entropy, with the original neuton transformed into more complex elements. In the light of present knowledge the creation of matter involves only the creation of electron pairs and this, as already shown, involves the degradation of energy. The whole process of cosmic evolution, therefore, appears to be governed by synthesis from the simple to complex and by the gradual transformation of nuclear energy into heat.

Note added in proof.—In particular the reactions

$$H_1^2 + H_1^2 \rightarrow H_1^3 + \overset{\nearrow}{p}; \quad H_1^2 + H_1^2 \rightarrow He_2^3 + \overset{\nearrow}{n}; \quad \text{and} \quad Li_3^7 + p \rightarrow \overset{\nearrow}{\alpha} + \overset{\nearrow}{\alpha}$$
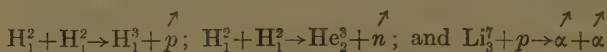
occur at accepted "main sequence" stellar temperatures, as it has been shown that the threshold energies for these reactions are as low as 20,000 e.v. and 13,000 e.v. (von Traubenberg, *Naturwiss.* v. 21, p. 26). In consequence protons and α particles, as well as neutrons of very high energy, exist in stars, and by their interaction with other nuclei produce all the transmutations suggested. These reactions probably play an important part in determining the relative abundance of the light elements. However, the fundamental synthesis process is by neutron capture, and it must be concluded that the neutron is the fundamental material particle, protons being mainly produced within nuclei by β radioactivity rather than by direct addition to nuclei as suggested by R. d'E. Atkinson.

LXXVI. *Raman Effect and the Complexity of the Mercurous
and Thallous Ions. By* LEONARD A. WOODWARD, *B.A.,
Ph.D.**

Introductory.

THERE is considerable physico-chemical evidence † in
support of the view that in solution the mercurous
ion does not exist in the simple form Hg^+, but in the
double form Hg_2^{++}. Drucker ‡ has also explained the
results of physico-chemical measurements on thallous
nitrate solutions by supposing that the thallous ion
exists to a considerable extent in the double form Tl_2^{++},
and that, in addition, the salt is only partially ionized.

The Raman effect offers a very direct method of
distinguishing between a monatomic and a diatomic ion ;
for the former will obviously show no Raman frequency,
whereas the latter will show a single frequency corres-
ponding to the mutual oscillation of the two atoms. The
present paper gives an account of investigations of the
Raman effect of mercurous nitrate and thallous nitrate
solutions.

Experimental Procedure and Results.

A modified form of Wood's arrangement was used §.

To prevent hydrolysis, the mercurous nitrate was
dissolved in 3N nitric acid by shaking at room-temperature.
After filtering, a little more 3N nitric acid was added to
the saturated solution to prevent any possibility of its
crystallizing out during the experiments. The con-
centration (determined by oxidizing a sample to mercuric
with concentrated nitric acid and titrating with thio-
cyanate) was found to be 0·62 gm. atom Hg per litre.

The best Raman spectra were obtained with exposure
times of 2 and 3 hours respectively. On each plate a
copper arc spectrum was recorded for comparison. The
wave-lengths of the Raman lines were determined from
the known Cu lines by interpolation, using the simplified

Hartmann formula. Tests on the Cu lines showed that the error of this method was less than ± 0.2 Å.U. for sharp lines.

The results obtained are given in Table I.

TABLE I.

Mercurous Nitrate Solution.

Raman line.		Exciting line.		$\Delta\nu$ in cm.$^{-1}$	Species.
λ in Å.U.	ν in cm.$^{-1}$.	λ in Å.U.	ν in cm.$^{-1}$.		
4225·5	23659	4046·8	24705	1046	NO_3'
4259·5	23470	4077·8	24516	1046	NO_3'
4326·2	23108	4358·3	22938	170*	Hg_2^{++}
4390·5	22770	4358·3	22938	168	Hg_2^{++}
4500·2	22215	4358·3	22938	723	NO_3'
4566·1	21894	4358·3	22938	1044	NO_3'

* Anti-Stokes line.
   Mean $\Delta\nu$-values : NO_3', 1046 (strong), 723 (weak) ; Hg_2^{++}, 169 cm.$^{-1}$ (strong).

Thus, in addition to the Raman bands of water (not included in Table I.) and the well-known lines of the nitrate ion ($\Delta\nu = 1046$ and 723 cm.$^{-1}$), we have a single strong frequency $\Delta\nu = 169$ cm.$^{-1}$ which we ascribe to the Hg_2^{++} ion. On the spectra this frequency appeared both as Stokes and anti-Stokes lines. In Table I. only the two lines excited by Hg 4358·3 are included. The analogous Stokes line excited by Hg 4046·8 lies close to Hg 4077·8 ; the analogous anti-Stokes line excited by Hg 4046·8 could also be seen on the plates.

For the experiments with thallous nitrate a nearly saturated aqueous solution of the salt (concentration about 0·32 gm. atom Tl per litre) was used. Several Raman exposures up to 20 hours' duration were made, but none of the plates showed any Raman line other than those due to the nitrate ion. The observed values for the strongest of the NO_3' lines are given in Table II. The mean $\Delta\nu = 1046$ cm.$^{-1}$ is exactly the same as is found for all solutions containing the NO_3' ion (*cf.* Table I.).

Discussion of Results.

1. *The Mercurous Ion.* — The Raman frequency $\Delta\nu = 169$ cm.$^{-1}$ observed in mercurous nitrate solution may be ascribed with certainty to the double form Hg_2^{++} of the mercurous ion, and provides direct proof that the ion exists in this form in solution.

In this connexion reference may be made to the results of Krishnamurti [*] on the Raman effect of mercurous nitrate crystals. In addition to frequencies due to the nitrate ion, he observed a frequency $\Delta\nu = 174$ cm.$^{-1}$. This he supposed to be a lattice frequency, by analogy with a frequency of about the same magnitude which he observed with lithium nitrate crystals, but which did not

TABLE II.

Thallous Nitrate Solution.

Raman line.		Exciting line.		$\Delta\nu$ in cm.$^{-1}$	Species.
λ in Å.U.	ν in cm.$^{-1}$.	λ in Å.U.	ν in cm.$^{-1}$.		
4225·8	23658	4046·8	24705	1047	NO_3'
4566·3	21893	4358·3	22938	1045	NO_3'

Mean $\Delta\nu$-value : 1046 (strong).

appear at all with concentrated lithium nitrate solution. The present investigation shows that with mercurous nitrate this frequency, unlike that of lithium nitrate crystals, persists strongly in solution, and cannot, therefore, be a lattice frequency.

From the observed value $\Delta\nu = 169$ cm.$^{-1}$ we can calculate at once the force-constant f of the link between the two Hg atoms in the ion $(Hg—Hg)^{++}$. This is given [†] by the equation $f = C\mu(\Delta\nu)^2$, where μ is the reduced mass. If $\Delta\nu$ is expressed in cm.$^{-1}$, the masses in units of atomic weight, and f in dynes per cm., the constant C is given by $C = 4\pi^2c^2/N = 5\cdot863 . 10^{-2}$ (c = velocity of light, N = Avogadro's number). Since the different frequencies corresponding to the different isotopes are not resolved, we

[*] Indian Journ. Phys. v. p. 1 (1930).
[†] Kohlrausch, ' Der Smekal-Raman-Effekt,' Berlin, 1931, p. 154.

may put $Hg=200\cdot6$. Hence we obtain $f=1\cdot68.10^5$ dynes per cm. This value is somewhat lower than is found for other single links, for which f lies between 2.10^5 and 6.10^5 dynes per cm. * ; but the fact that it is so near is evidence in support of the allocation of the frequency to the Hg_2^{++} ion.

2. *The Thallous Ion.*—If the thallous ion existed in the double form Tl_2^{++}, and if the concentration of this form were sufficiently high, we should expect to observe a Raman frequency. Its magnitude would be approximately the same as that of Hg_2^{++} if the link between the thallium atoms were single, or about $\sqrt{2}$ times greater if the link were double. Drucker (*loc. cit.*) gave the values $2\cdot1$ and $0\cdot27$ respectively for the mass action constants of the equilibria $2Tl^+\rightleftharpoons Tl_2^{++}$ and $TlNO_3\rightleftharpoons Tl^++NO_3'$. Assuming these to hold for our concentration, we should expect about $\frac{1}{4}$ of the thallium to be present as Tl_2^{++} and about $\frac{1}{3}$ as undissociated $TlNO_3$. Actually the Raman spectra obtained give no evidence for either Tl_2^{++} or $TlNO_3$. As far as Tl_2^{++} is concerned this negative result has a definite meaning by contrast with the positive result for Hg_2^{++}. A strong line was obtained for Hg_2^{++} in two hours at a salt concentration of $0\cdot62$; no trace of a line was obtained for Tl_2^{++} in 20 hours at a salt concentration of $0\cdot32$. Assuming that the whole of the mercurous ion is in the double form, and that the intrinsic intensity of the Raman line of Tl_2^{++} would be the same as that of Hg_2^{++}, we can deduce that the fraction of thallium in the form of Tl_2^{++} is certainly not more than $\frac{1}{10}$ and probably much less.

As pointed out by Sidgwick †, the formation of a stable thallous ion is an example of the inertness of the N_1 pair of electrons as far as ionization is concerned. The present investigation, which indicates that the double form of the ion (if it exists at all) can only be present in small concentration relative to the simple form, shows that the tendency of the N_1 electrons to be shared, which leads to the formation of $(Hg—Hg)^{++}$, does not extend to thallium. The pair of N_1 electrons in the simple thallous ion evidently possesses a greater stability than the single N_1 electron which would be present in a simple mercurous ion. The

* For collected data see Kohlrausch, *loc. cit.*

† ' Electronic Theory of Valency,' Oxford, 1927, pp. 178–181.

double ion $(Hg—Hg)^{++}$ appears to be quite unique in that it presents the only case of a covalent link between two metallic atoms.

Summary.

A nearly saturated solution of mercurous nitrate in 3N nitric acid shows, in addition to the bands of water and lines due to NO_3', a strong Raman frequency $\Delta\nu = 169$ cm.$^{-1}$ which is ascribed to the double form $(Hg—Hg)^{++}$ of the mercurous ion. The Raman spectrum of a nearly saturated solution of thallous nitrate gives no evidence of a double ion Tl_2^{++} or of undissociated $TlNO_3$ molecules. It is deduced that the Tl_2^{++} ion, if it exists, must have a concentration less than would correspond to 10 per cent. of the total thallium present.

University College, Nottingham.
June 1934.

LXXVII. *An Experiment relating to the Thermal and Electrical Theories of Spark Ignition.* By J. D. MORGAN, *D.Sc.* *.

THE gaseous molecules in and around an electric spark derive their motion from two agencies, namely, heat and the action of the electric field in which the spark occurs. If it can be assumed that activation of gaseous molecules results, whether wholly or in part, from molecular collisions, then it appears a reasonable supposition that the activation caused by an electric spark may be due to molecules moving under the action of either of the two agencies above mentioned. The experiment now to be described was designed to test this supposition.

The experiment is based on two facts which are already known. The one is that a wire which is heated electrically to a temperature below incandescence, and which produces no observable electrification in its immediate neighbourhood, can cause the constituents of an inflammable gas mixture to combine †. The other is that such a mixture

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can be exposed to a strong electric (but sparkless) discharge from a needle point for a long time without any sign of combustion becoming apparent. It was thought, however, that less thermal energy might suffice to bring about combustion in the mixture if it were supplemented by a strong electric discharge. The underlying idea of the experiment is, therefore, to make use of separate and independently controllable thermal and electrical agencies operating simultaneously in the same region of the gas mixture.

There was arranged in a small chamber a a small-diameter coil b of thin platinum wire. This was heated by an electric current. About $0.25''$ away from the wire
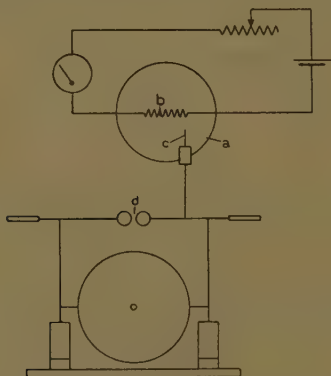
was placed the point of an insulated sewing needle c. The point was situated near one end of the wire to minimize the cooling effect on the wire of the wind from the point. The needle was at first attached to one pole of a Wimshurst machine d as shown in the diagram. The gas in the chamber consisted of a 5 per cent. mixture of Birmingham coal gas and air, this very weak mixture being more convenient to experiment with than one which could be readily ignited. The reaction in the gas proceeded without apparent flame, and the amount of the reaction was measured by a small water-pressure gauge contained in a U-tube attached to the combustion chamber. After each experiment the chamber was evacuated and a new charge was admitted from a storage bottle, the initial

condition of the charge in the chamber being at atmospheric pressure and temperature.

The procedure followed was in the first place to find the current required in the wire to cause reaction in the gas. After closing the wire circuit, the current in it was gradually increased. This action was accompanied by an increase of pressure, as shown by the gauge. There was no visible heating of the wire. When the current value was sufficiently increased (still without causing incandescence of the wire) the reaction commenced. Then the pressure gauge showed a further increase of pressure due to the heat of the reaction, and the wire glowed faintly. After reaching a maximum, the pressure began to fall, due to the reduction of volume of the gas in consequence of the reaction, and the pressure continued to fall and the wire to glow with diminishing brightness until the reaction ceased. In this way there was found the value of the current required to start the reaction. For a given wire and gas mixture the value was a very definite one. It was not, however, the same for all wires, but varied with the diameter of the wire and the pitch or spacing of the convolutions. A typical current value was 0·56 amp.

The experiment was then repeated on another charge with the current fixed at some lower maximum value than 0·56 amp., and by means of the Wimshurst machine the needle point was electrified, the potential difference between the needle point and the wire being between 3 and 4 kv. A faint glow could be seen on the needle point, and in the dark a very faint and thin glow could be seen extending across the gap between the needle point and the wire. To limit the voltage on the point the poles of the Wimshurst machine were brought together to form a gap d, which was set to break down when the voltage between the needle point and the wire exceeded 4 kv., this voltage being measured in the initial adjustment of the apparatus by means of an electrostatic voltmeter. During the course of the experiments sparks occurred intermittently at d.

After a few trials it was found that no supplementary effect could be obtained from the electric discharge from the needle point when the current in the wire was less than 0·52 amp. But when the current was adjusted to 0·54 amp. it was found that reaction could be started

in the gas with the needle point electrified, whereas
with the needle point dead the reaction could not be
started by the wire until the current was increased to
0·56 amp. The experiments were repeated many times
with the same very definite result. It appeared, there-
fore, that whilst the heat of the wire was the predominant
agent in causing activation of the gas this agent was
capable of being supplemented (though feebly) by the
electric discharge from a needle point. The effect was
independent of the polarity of the needle.

It was then decided to see whether a stronger effect
could be obtained from the needle point by increasing
the voltage applied to it. For this purpose the gap *d*
was opened out so that no spark would occur at it, and
the avoidance of sparks between the needle point and
the coil was effected by suitably regulating the rate
of operation of the Wimshurst machine. The surprising
result was then obtained that the discharge from the needle
point produced no supplementary effect on the heat
of the wire, except when a spark occurred between the
needle point and the wire. This spark was very thin,
and neither a single spark nor a succession of sparks
was by itself able to produce any appreciable reaction
in the gas, but it did have the effect of starting the
reaction when the current in the wire was at about
0·54 amp.

The experimental condition first described was then
reverted to, and the fact was definitely established that
with sparking at *d* the discharge at the needle point
supplemented the heat of the wire coil, but with no
sparking at *d* there was no supplementary effect.

It was then remembered that Wynne Williams had
found * that when a needle point is connected to one
of the secondary terminals of an induction coil it gives
off radiation, and that in certain experiments of the
writer † this effect was not obtained when the needle
point was electrified in a steady manner. It seemed
probable, therefore, that in the first experiment there was
present an effect which was due to radiation and not
to the simple movement of ionized molecules in the
field between the needle point and the wire. The needle
point was then connected to one pole of an induction

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* C. E. Wynn Williams, Phil. Mag. vol. i. p. 353 (Feb. 1926).
† J. D. Morgan, Phil. Mag. vol. iiv. p. 91 (July 1927).

coil, the primary current being adjusted so that no spark passed from the needle to the wire. The results first described were then obtained again, namely, that with the needle point electrified, 0·54 amp. in the wire sufficed to start reaction in the gas mixture. This suggested that the first result was due to a pulse of radiation given off by the needle point when a spark occurred at *d*.

It then remained to test the suggestion, and to do this a wire gauze was placed in the chamber between the needle point and the wire, with one end attached to the circuit containing the wire. This had the effect of trapping the ionized molecules and letting only the radiation from the needle point reach the wire. The results were similar to those first obtained. They were, however, a little less definite. The presence of the gauze appeared to weaken slightly the action of the discharge from the point.

The conclusion to be drawn from these experiments is that under the conditions described the activating effect of the heat of the wire could not be supplemented by ionized molecules moving in the neighbourhood of the wire under a strong electric field, but that such effect could be supplemented by radiation of the kind given off by a needle point when subjected to a pulse of electrical pressure.

The conclusion is of interest in connexion with certain experiments of which accounts have recently been published. Tchang Te-Lou has stated * that he was able to maintain the running of a petrol engine without the usual igniting spark, provided a corona discharge was obtained from the electrified pole of the sparking plug. The writer suggests that the explanation of this result is that the gaseous mixture was raised by compression in each cycle to very near the ignition temperature, and that the effect of the heat of compression was supplemented by a pulse of radiation from the sparking plug. Another experiment with which the writer's experiment may be compared is one by Bernard Lewis and C. D. Kreutz †, in which they found that a methane-air mixture could be ignited at a lower temperature than

* Tchang Te-Lou, *Comptes Rendus,* vol. cxcviii. p. 542 (Feb. 5th, 1934).

† Bernard Lewis and C. D. Kreutz, Journal of Chemical Physics. vol. i. no. 1 (Jan. 1933).

the normal when an inert gas which had, immediately
prior to its introduction to the chamber containing the
combustible mixture, been passed through a strong
electric spark. The results of the writer's experiment
appear to warrant the suggestion that the inert gas was
in some way energized in a manner which enabled it to
act on the combustible gas in a similar manner to radiation.
It may be, too, that the well-known experiments of Finch
and Coward *, and Finch and Thompson †, are capable
of explanation in terms of heat and radiation.

It must be admitted, however, that the results described
in this paper are perplexing. But whatever might be
the final interpretation of the experiments, they do show
definitely that under the conditions described the action
of a hot wire in activating a gas can be feebly supple-
mented by radiation of the kind discovered by Wynne
Williams.

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LXXVIII. *The Theory of ultra-short Wave Generators. By*
    E. W. B. GILL, *B.Sc., M.A., Fellow of Merton College,*
    Oxford ‡.

ALTHOUGH it is now fourteen years since Barkhausen
    and Kurz discovered a means of generating un-
damped oscillations of very short wave-length, and although
they have been studied by very many investigators §,
there is still no generally accepted theory as to how these
oscillations are maintained. It seems worth while,
therefore, to collect some of the main experimental
results and see what deductions appear inevitable from
them.

One of the most usual methods of producing these short
waves is shown in fig. 1. Lecher wires $L_1 L_2$ are joined
to the grid G and anode P of a 3-electrode gas free valve ;
at the other end is a large capacity C.

    * Finch and Coward, Proc. Roy. Soc. A, vol. cxi. (1926); and A,
vol. cxvi. (1927).
    † Finch and Thompson, Proc. Roy. Soc. A, vol. cxxxiv. (1931).
   ‡ Communicated by Prof. J. S. Townsend, M.A., F.R.S.
    § A very complete list of these researches is given by E. C. S. Megaw.
Journ. Inst. Elect. Eng. p. 313 (April 1933(.

The grid is kept at a potential $+V$ with respect to the filament, and the anode at the same potential as the filament by leads brought in on the two sides of C.

With this arrangement it is found that for a suitable value of V and proper heating of the valve filament oscillations will be produced in the circuit P, L_1, C, L_2, G. When no oscillations are taking place the anode current as indicated by the milliammeter A is practically zero, but the occurrence of oscillations is accompanied by an appreciable anode current.

The oscillatory circuit comprises the capacity PG between anode and grid, and the distributed inductance and capacity of L_1L_2 (and the leads inside the valve). If the capacity C is large the alternating potential across

Fig. 1.
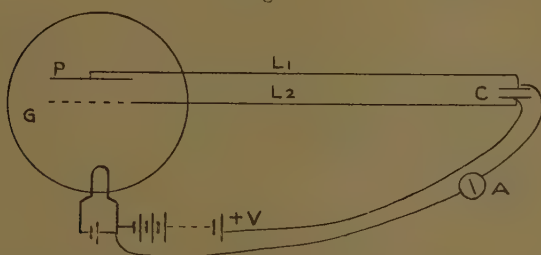
it is negligible for short waves, and its terminals may be regarded as nodes of potential oscillation. In fact, so far as oscillations are concerned it may be regarded as a short circuit.

The wave-length of the oscillation set up has to be one of the possible modes of oscillation of this circuit ; it is very rare for the fundamental oscillation to occur, but which particular mode of oscillation is generated depends on V. For any such mode there is a definite value of V and also a definite filament temperature for which the amplitude of the oscillations is a maximum.

It is not generally known that oscillations can be produced equally well if the Lecher wires are joined to the filament and anode instead of to grid and anode. The circuit is shown in fig. 2 ; here, owing to the necessity of having two filament leads the Lecher wire L_2 has to be replaced by two wires parallel and close together. The

condenser C requires slight modification as shown. The oscillatory circuit is the same as in fig. 1, except that the concentrated capacity in the valve is that between filament and anode in place of that between grid and anode.

The capacity between the filament and anode may be virtually regarded as two capacities in series, the first composed of filament and grid, the second of grid and anode. If these two capacities are equal the grid will be a node of potential for the oscillations. With the valve employed this was found to be practically the case, since it was found that no appreciable oscillation could be

Fig. 2.
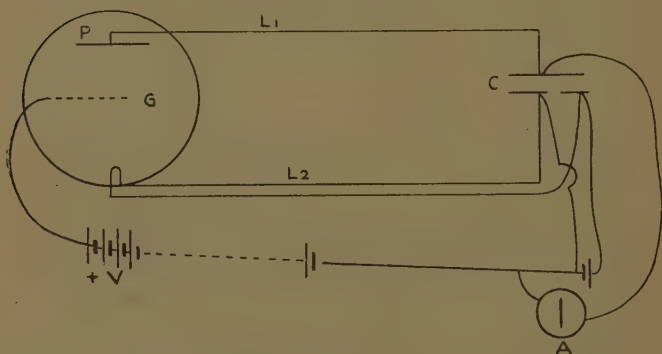
detected in the grid lead. The fact that it is possible to maintain oscillations with the grid at a potential node, which is not the case in the more usual circuit of fig. 1, throws a good deal of light on the theory of the oscillations.

As mentioned above, when oscillations are occurring an appreciable anode current is set up and the current from the filament through the valve must therefore divide, part flowing to the grid and the rest to the anode. The former current flows through the high tension battery V and returns to the filament along L_2 from C. In fig. 2 this current enters the oscillatory circuit at a node of potential C and leaves it at another node G and can therefore have no effect at all on the oscillations, neither damping them nor regenerating them. It follows

that the oscillations must be maintained by the current to the anode alone (which is contrary to the common idea that the anode current in this type of oscillation causes damping).

The only available source of energy, however, in the circuit is the grid battery V, and the problem therefore reduces to finding how this battery, which is connected to grid and filament, can transfer energy to the anode through the action of the valve. This battery can only do work if current passes through it, that is, it can only give energy directly to the electrons which pass from the filament to the grid. If, therefore, it transfers energy to the anode circuit the electrons which pass from the filament to the anode must in some way acquire this energy from the electrons which end up on the grid.

In the static case when there are no oscillations the anode current is zero and the general motion of the electrons is an acceleration from the filament till they pass through the grid, then a retardation till they reach the surface of the anode, where they momentarily come to rest, since it is at the same potential as the filament (velocities of emission from the filament are neglected) ; they then turn back and perform a similar motion in the reverse direction, passing close to the filament, and after a few transits backwards and forwards between anode and filament are ultimately caught on the grid (possibly a very few return to the filament).

Under normal circumstances the mutual repulsions of these electrons merely modifies the original electric field due to V, but it does not result in any interchange of energy between the electrons, *i. e.*, every electron passing a point where the potential is V_0 has the same energy eV_0; they all come to rest at the surface of the anode and none have sufficient energy to reach it, and they all ultimately hit the grid with energy eV, where the whole work done on them by the battery is transformed into grid heating.

If, on the other hand, there are any fluctuations in the currents crossing the valve it is possible for an electron to acquire energy from another, provided the space charge in the vicinity of the anode is saturated. This is discussed fully in previous papers *, and only a short summary will be given here.

The space charges due to the currents in the grid-anode

* E. W. B. Gill, Phil. Mag. p. 993 (May 1925) ; and p. 859 (May 1928).

space modify the electric field set up by V, and in particular reduce the force just outside the anode which attracts the electrons back towards the grid. This results in there being a limit to the size of the current which can penetrate to the surface of the anode, the limit being reached when the force at the anode is reduced to zero. Call this limiting current i. If a current i_1 larger than i is passed in through the grid the electrons comprising it do not get up to the anode, but come to rest and turn back at some small distance from it.

So long as i or i_1 do not vary no interchange of energy between electrons is possible, but during a change from i to i_1, energy is transferred. The first set of electrons in the larger current i_1 on their arrival near the anode, cause a momentary reversal of field there and repel the last set of electrons of the current i on to it.

The latter each gains energy eV_1, say, from the former and transfer it to the anode, the former each, having lost this amount of energy, hit the grid with reduced energy $eV - eV_1$, and the whole work eV of the battery is no longer wasted in heating the grid, but the portion eV_1 is transferred to the anode circuit. It should be noted that the anode will receive this pulse of current even if its potential is negative to the filament by any amount less than V_1.

If the oscillatory circuit attached to the valve has a periodic time of oscillation T then an oscillation will be maintained in it if a succession of pulses arrive at the anode at intervals T.

The last problem, therefore, to be solved is how the arrival of one pulse causes the arrival of further pulses at equal intervals.

In the static case the flow of electrons to and fro across the valve is perfectly steady, giving rise to the above current i. The larger current i_1 may be regarded as a sort of compression, the electrons in it being more per cubic centimetre than for the normal current i. When this compression reaches the anode a portion of it is forced on to the anode, and the returning stream owing to this loss has less electrons per c.c. than the normal, *i. e.*, it may be regarded as a rarefaction.

It is necessary, therefore, that this rarefaction should at some point in its path set up a fresh compression to move to the anode.

There appear to be two ways in which this may occur, depending on the dimensions of the valve.

If the grid is close mesh the transformation occurs at the grid. The returning rarefaction on arrival at the grid causes a compression to pass through the grid in the opposite direction and move to the anode, after which the process repeats; the interval at which pulses reach the anode is twice the time taken for an electron to move from the anode to grid. This time depends on $\sqrt{V}$, and by choosing the proper value of V the pulses can be made to arrive at a time interval T.

This case has been discussed fully in a previous paper *.

For such a valve, if λ is the wave-length of the oscillation, V the value of the grid volts, and i the grid current for optimum oscillation, then $\lambda^2 i/\sqrt{V}$ is constant; a relation obtained independently and experimentally verified by Rostagni †.

In this case the space between filament and grid is not saturated.

If the grid is open mesh the control at the grid ceases to be effective. The only place where the returning rarefaction can operate is when it is in the vicinity of the filament. The arrival of the rarefaction must cause a momentary increase in the number of electrons leaving the filament. But this can only occur if the filament grid space is saturated. This is, of course, the usual condition of a valve for most wireless purposes. Some of the electrons emitted from the hot filament return to it after traversing a very short distance, while the remainder traverse the valve. The arrival of the rarefaction momentarily decreases the number returning to the filament and consequently increases the number traversing the valve. The time interval between the arrival of successive pulses is now twice the time for an electron to pass from filament to grid. In this case the above relation between λ, i, and V is not necessarily true, and is in general replaced by λ^2 V equals constant

It should be noticed also that in this case both the spaces, filament-grid and grid-anode, are saturated.

Note.—Some writers are of the opinion that there are two types of short wave-oscillation, which they call

* Gill, Phil. Mag. p. 843 (Oct. 1931).
† A. Rostagni, *Atti della R. Acad. di Torino*, xvi. pp. 123, 217, and 383 (1931).

the B-K type and the G-M type. The latter are the ones discussed in this paper, the former are supposed to be an electron oscillation inside the valve and quite independent of the external circuits.

It is very difficult to believe that such exist; it would appear impossible for such oscillations not to induce oscillatory potentials on the electrodes, and even if no symmetrical oscillatory circuit is placed outside, the leads to the various electrodes have natural periods of short wave-length some mode of which will be set in oscillation and the result would be a G-M type of oscillation.

If, on the other hand, it were possible for all the electrodes to remain at fixed potentials it would appear to be impossible for the grid battery to supply any energy to maintain the oscillations.

I am very grateful to Professor Townsend, in whose laboratory the experiments were conducted, for advice and criticism.

LXXIX. *On the Distribution of Energy in the Ultra-Violet Solar Spectrum as inferred from the Photochemical Theory of the Ozone Equilibrium in the Earth's Atmosphere. By* D. EROPKIN *.

ASSUMING that the mean annual value of the ozone content is constant for each geographical latitude, the mean value of each side of Chapman's † equations for the ozone variation can be equated to zero, *i. e.*,

$$\frac{dn_1}{dt} = 2\sigma_2 n_2 I + \sigma_3 n_3 I - 2k_{11}n_1{}^2 - k_{12}n_1 n_2 - k_{13}n_1 n_3 = 0,$$
$$\frac{dn_3}{dt} = k_{12}n_1 n_2 - \sigma_3 n_3 I - k_{13}n_1 n_3 = 0, \qquad (1)$$

where each term denotes the annual mean value instead of (as originally) the instantaneous value.

The term $k_{33}n_3{}^2$ is rejected in the second of the given equations.

Substituting for the first of the equations the sum of the first and the second, and dividing both equations by $n_2{}^2$, we shall have

$$\left.\begin{array}{c} \sigma_2\rho - k_{11}\nu_1{}^2 - k_{13}\nu_1\nu_3 = 0, \\ k_{12}\nu_1 - k_{13}\nu_1\nu_3 - \sigma_3\nu_3\rho = 0, \end{array}\right\} \quad \cdots \quad (2)$$

where ρ, ν_1, and ν_3 are given by

$$\nu_1 = \frac{n_1}{n_2}, \quad \nu_3 = \frac{n_3}{n_2}, \quad \rho = \frac{I}{n_2} \cdot \cdots \quad (3)$$

By eliminating ν_1 from the equations (2) we obtain the dependence between ρ and ν_3 in the form of a cubic equation :

$$\nu_3{}^3 + (\alpha - \beta\rho)\nu_3{}^2 - \gamma\nu_3 + \delta = 0. \quad \cdots \quad (4)$$

The coefficients of the equation (4) are expressed as follows in terms of the coefficients of the system (2) *.

$$\alpha = \frac{\sigma_2}{\sigma_3} - \frac{k_{12}}{k_{13}}, \quad \beta = \frac{k_{11}}{k_{13}{}^2}\sigma_3, \quad \gamma = 2\frac{k_{12}}{k_{13}}, \quad \delta = \left(\frac{k_{12}}{k_{13}}\right)^2 \frac{\sigma_2}{\sigma_3}. \quad (5)$$

If instead of ν_3 and ρ we consider the quantities $\nu' = p\nu_3$ and $\rho' = q\rho$, where p and q are some constant factors, the equation (4) will be replaced by the analogous equation

$$\nu'^3 + (\alpha' - \beta'\rho')\nu'^2 - \gamma'\nu' + \delta' = 0, \quad \cdots \quad (6)$$

where

$$\alpha = \frac{\alpha'}{p}, \quad \beta = \beta'\frac{q}{p}, \quad \gamma = \frac{\gamma'}{p^2}, \quad \delta = \frac{\delta'}{p^3} \cdot \cdots \quad (7)$$

In order to obtain the coefficients of the equation (4) we shall consider how the ozone content depends upon the latitude.

Using Dobson's data, the table (p. 840) gives the locality of the observations, the geographical latitude ϕ, the mean annual ozone content ν' given in centimetres (taken from Dobson's curves), and the mean annual intensity of the solar radiation ρ' in Angot units (Milankovitch). Each pair of values ρ' and ν' inserted in the equation (6)

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* It is to be noted that the coefficients α, γ, and δ depend only on the ratios $\frac{\sigma_2}{\sigma_3}$ and $\frac{k_{12}}{k_{13}}$. By eliminating these we obtain the equation

$$\alpha = \frac{\gamma^2}{4\delta} - \frac{2\delta}{\gamma}.$$

From the empirical material we have α, γ, and δ ; this equation can be employed to verify the value obtained.

gives one *conditional* equation for the determination
of the coefficients α', β', γ', and δ' in the form

$$\delta' - \nu'\gamma' - \rho'\nu'^2\beta' + \nu'^2\alpha' = -\nu'^3.$$

No.	Observatory.	ϕ^0.	ν'cm.	ρ'.
1	Lerwick.	60	0·300	0·1737
2	Lindenberg.	52·5	286	2002
3	Oxford.	52	286	2019
4	Valentia.	52	297	2019
5	Arosa.	47	262	2189
6	New Zealand.	−44	285	2287
7	California.	35	270	2556
8	Egypt.	30	228	2683
9	Chile.	−22	215	2852
10	India.	10	0·202	0·3011

The corresponding normal system has the form

$$
\begin{array}{ccccc}
\delta'. & \gamma'. & \beta'. & \alpha'. & l. \\
[l] & -[\nu'] & -[\rho'\nu'^2] & +[\nu'^2] & -[\nu'^3] \\
 & [\nu'^2] & +[\rho'\nu'^3] & -[\nu'^3] & +[\nu'^4] \\
 & & +[\rho'\nu'^4] & -[\rho'\nu'^4] & +[\rho'\nu'^5] \\
 & & & [\nu'^4] & -[\nu'^5]
\end{array} \quad (8)
$$

Eight conditional equations are formed, one for each station
except nos. 4 and 6, which are inconsistent with the
general " run " of the relation between ρ' and ν'.

The solution of the corresponding system of normal
equations gives the following values of the desired
coefficients * :

$$\alpha' = +3·750, \quad \beta' = +4·639, \quad \gamma' = +1·9235, \quad \delta' = 0·2934.$$

According to the previous data for the ozone layer
$\nu' = 0·3$ cm. corresponds to the ozone content $\nu = \dfrac{1}{1500}$
($p = 450$). This value corresponds to a height h of
50 km. for the ozone layer. But the recent data of
Götz, Meetham, and Dobson suggest that this value of
p should be trebled, quadrupled, or even more. Hence,
leaving aside for the present the factor q and the coefficient
β connected with it, we find for the other coefficients

$$\alpha = 8·3 . 10^{-3}; \quad \gamma = 9·5 . 10^{-6}; \quad \delta = 3·2 . 10^{-9}.$$

* More detailed calculations are given in Bull. Commission récherches
du Soleil, Acad. Sci. U.R.S.S. N. 9.

From the last equations (5) we obtain

$$\frac{k_{12}}{k_{13}} = \frac{2\delta}{\gamma} \quad \text{and} \quad \frac{\sigma_2}{\sigma_3} = \frac{\gamma^2}{4\delta},$$

or in numbers

$$\frac{k_{12}}{k_{13}} = 0.67 \cdot 10^{-3} = \frac{1}{1500} \; ; \; \frac{\sigma_2}{\sigma_3} = 7.05 \cdot 10^{-3}$$

$$= \frac{1}{140} \quad \text{for } h = 50 \text{ km.}, \quad . \quad . \quad (9)$$

and

$$\frac{k_{12}}{k_{13}} \simeq 10^{-2} \; ; \; \frac{\sigma_2}{\sigma_3} \simeq \frac{1}{600} \quad \text{for } h = 20 \text{ km.} \quad . \quad (10)$$

The energy curve for black body radiation gives $\frac{\sigma_2}{\sigma_3} = 1 : 600$. It is to be noted that the inferred value of $\frac{\sigma_2}{\sigma_3}$ will vary inversely as p.

Thus, on the basis of the photochemical ozone theory we conclude that the sun's ultra-violet spectrum corresponds to Planck's curve if the ozone mean height is 20 km., but that the sun's spectrum would be approximately five times richer in ultra-violet energy if the height of the ozone layer is 50 km.

On general physical considerations the distribution of ultra-violet energy according to Planck's curve seems quite probable ; the corresponding height of 20 km. accords with the preliminary communication of Götz, Meetham, and Dobson.

The above-mentioned considerations represent only a first attempt to calculate the distribution of the energy in the ultra-violet sun spectrum ; the inexactitude of the results is due to the uncertainty in the value of p.

We hope that the coming stratosphere flights will enable the energy curve in the ultra-violet solar spectrum and the value of p to be determined by actual measurements, so as to test the method as well as the estimates of the present note.

Academy of Science U.S.S.R.,
Solar Commission, Leningrad.
May 1934.

LXXX. *Notices respecting New Books.*

A Treatise on the Catalytic Action of Surfaces. By J. E.
NYROP. [Pp. 75.] (Levin & Munksgaard, Copenhagen,
1934.)

THIS " treatise " is, in reality, a short monograph devoted
to the consideration of processes occurring at catalytically
active surfaces. The author puts forward the view that the
catalytic action of metallic surfaces is determined mainly
by the electronic state of the metal. It is claimed that such
surfaces are responsible for the ionization of the reacting
molecules, and that the decrease in energy of activation,
which is characteristic of the adsorbed ions, is directly related
to the catalytic effects.

The author's views are said to permit of the systematic
treatment of catalytic effects in relation to the nature of the
surface, temperature, and pressure ; but there is not much
evidence to show that the actual behaviour of a metallic surface
can be predicted on the basis of the theory.

The Thermodynamics of Electrical Phenomena in Metals.
By P. W. BRIDGMAN. [Pp. vii + 200.] (New York : The
Macmillan Company, 1934. Price 16s.)

DURING the last fifteen years Bridgman has written a con-
siderable number of papers dealing with the thermodynamic
interrelations between thermoelectric and other electric
properties of metals. In this book the substance of these
is gathered together. In the discussion of thermoelectric
and related phenomena there are numerous pitfalls for the
unwary, and Bridgman has performed a useful task in under-
taking a thorough consideration of the relations which can
be deduced purely from arguments of a thermodynamic
type. These relations form a valuable set of controls on the
one hand of basic assumptions which may have been too
uncritically accepted, and on the other of the validity and
novelty of relations deduced by more detailed electronic
treatments. The relations obtained and the mode of presenta-
tion of the arguments have, moreover, an interest of their own.

Bridgman discusses thermoelectric phenomena, the Volta
effect, thermionic emission, cold emission under intense
fields, and the transverse thermo- and galvanomagnetic
effects, severely restricting himself to arguments of a very
general character. He then considers briefly the connexion
of the results with the electron theory of metals.

The discussion is somewhat detailed, particularly on fundamental points which are often slurred over. Though this serves to clarify the issues involved, it might be suggested that the book would have been even more useful if the main results obtained had been collected together and set forth succinctly. The reader has to keep alert throughout the journey if he is not to miss the views, and the views are slightly disappointing. This, however, to the reviewer at least, is a common characteristic of thermodynamic journeys for which the guide can hardly be held responsible.

The time is perhaps not yet ripe for a treatise on thermoelectric and related phenomena of the kind for which many physicists are hoping. For such a treatise, however, a fundamentally important chapter is provided by Bridgman's book, which will certainly be appreciated by all physicists interested in these phenomena.

Statics. By A. S. RAMSEY. [Pp. xi+296.] (Cambridge University Press, 1934. Price 10s. 6d.)

THIS book is a companion volume to the author's book on Dynamics published a few years ago, and is suitable for students in the higher divisions in schools and first-year university students. The subject is developed along the usual lines of a book on elementary statics, but special attention is given to graphical statics, friction, and virtual work. Chapters on flexible strings, the bending of rods, and force systems in three dimensions will be appreciated by more advanced students. More than a hundred worked examples are included in the text, and nearly five hundred problems (with answers) are given as exercises for the student. The book will be particularly useful to university scholarship candidates.

The Electromagnetic Field. By H. F. BIGGS. [Pp. viii+158.] (Oxford : Clarendon Press, 1934. Price 10s. 6d.)

THIS book is intended for students who are starting an honours course in physics. The subject is introduced from an elementary point of view, and the relevant vector algebra is developed as required together with the physical theory to which it is to be applied. The derivation of the most important electromagnetic relations is summarized in a table which shows clearly the connexion between the relations, and indicates those which are derived directly from experiment. Many applications of the theory are given in the book, and among the interesting topics in a chapter dealing with the energy in the field, the scalar and vector potentials, and the Poynting Vector are

accounts of the field of an accelerated charge, the scattering of light, and radiation pressure. The author develops his subject in terms of three dimensional space and independent time, but mentions the desirability of a more general and consistent scheme, which is the aim of his treatment, and which is attained in a final chapter on Special Relativity and the Electromagnetic Field.

The Differential Invariants of Generalized Spaces. By T. Y. THOMAS. [Pp. 240.] (Cambridge University Press, 1934. Price 21s.)

THE great success which attended the application of Riemannian or metrical geometry in relativity theory to the problem of gravitation has served to stimulate the study of the more general geometries of the spaces of affine connexion. The object in view has been to find some such space which would serve as a basis for a unified field theory of gravitation and electricity. Although this latter end has not yet been attained, a great theory of differential geometry has been built up during the last sixteen years, in the erection of which Prof. Thomas has himself taken no small part. He now gives us an admirable and lucid account of the whole subject of affine geometry from the purely analytical standpoint. Special attention is devoted to metrical geometry, the geometry of spaces of distant parallelism, Weyl geometry, and conformal spaces. Of projective geometry he treats of one case only, and leaves aside the most recent projective theories of Schouten and v. Danzig and of Veblen, which these authors have used in their unified field theories. It is difficult to signalize for special mention any part of this book, but the treatment and use of normal coordinates, the account of the problem of reducibility and equivalence of spaces, and of the theory of groups are of particular interest. The subject-matter is presented very clearly, but the use of small print for certain paragraphs is, at times, disconcerting. Thus, on p. 54 some essential definitions are printed in small type.

This book is certainly one that no relativist can do without, and it should give much food for thought and exercise a restraining influence on those who wish to embark on the construction of yet another unified field theory.
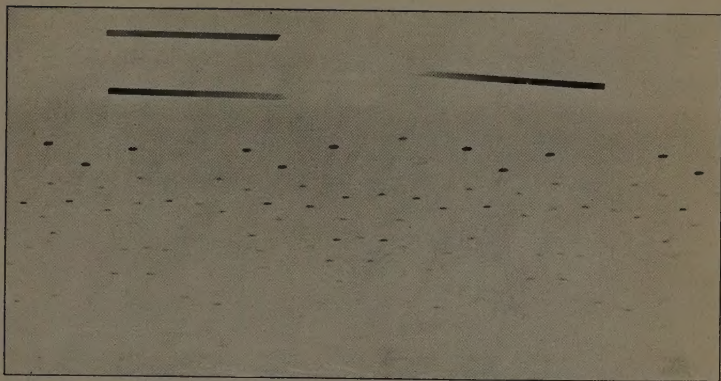
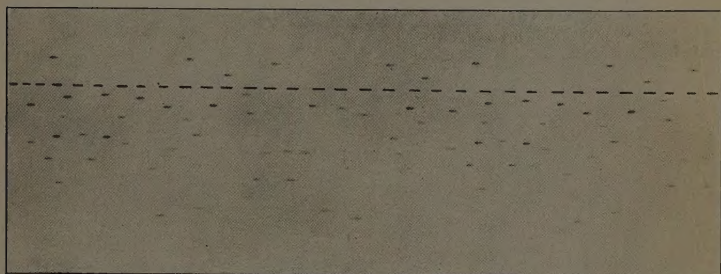*[The Editors do not hold themselves responsible for the views expressed by their correspondents.]*
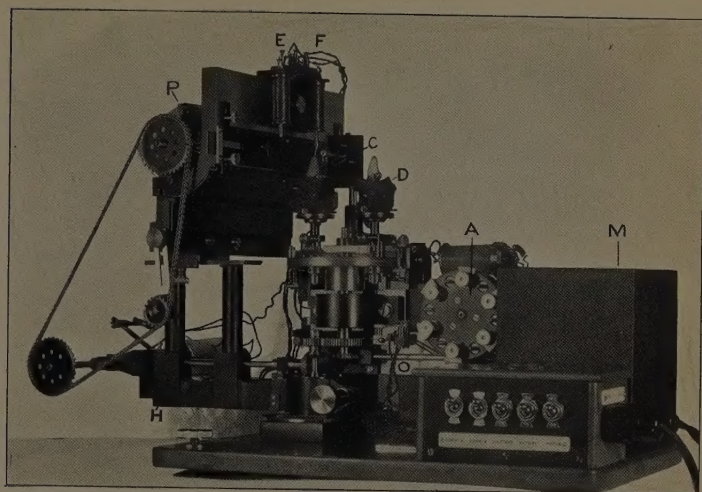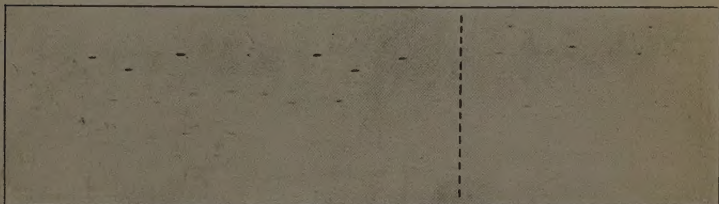
Two-crystal spectrometer—elevation.
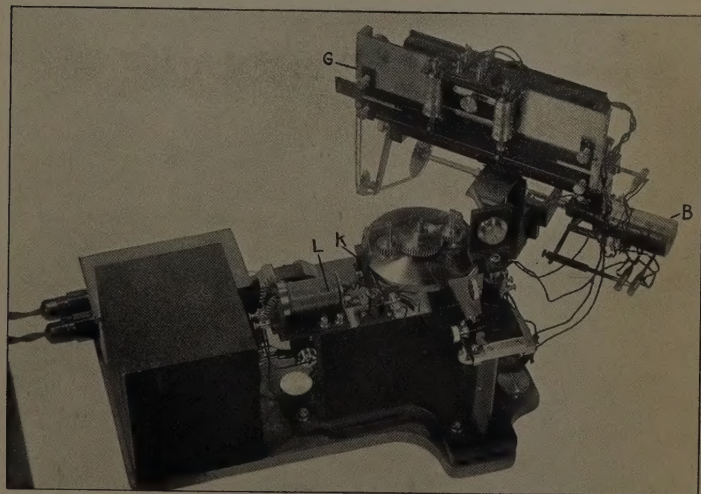
Two-crystal spectrometer—from above.

Robertson.

Phil. Mag. Ser. 7. Vol. 18, Pl. XVI.

(a) Unreduced single-crystal exposure, with calibration wedges. Camera at 60° to beam.

(b) As above, but strong reflexions reduced twelve times. Camera at 45° to beam.

(c) Two-crystal exposure.